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Electrochemical and spectroscopic studies on some pyridyl and morpholyl adducts of (*meso*-tetraphenylporphyrin)chromium(III) chloride

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Abstract. The electrochemical behaviour of the adducts $\text{Cr}(\text{TPP})\cdot\text{Cl}\cdot L$, where TPP = tetraphenylporphyrin; L = pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine or 4-picoline is reported and the relationship between reduction potentials, the electron band I transition and the binding energy of the Cr $2p_{3/2}$ level examined.

Based on criteria for the differences in oxidation potentials determined in acetonitrile by cyclic voltammetry and reduction potentials determined in DMSO, it is concluded that the adducts behave as normal metalloporphyrins. Further, variations for the different adducts are attributed primarily to different inductive effects from the heterocyclic axial groups. The adduct formed from 2,6-lutidine, however, shows anomalous behaviour which is attributed to a marked steric effect between the ligand and the porphinato-nitrogen atoms.

Keywords. (*meso*-Tetraphenylporphyrin)chromium(III) chlorides; base adducts; electrochemical behaviour.

1. Introduction

Previous studies on chromium porphyrins by spectroscopic techniques (Cheung *et al* 1976; Scheidt *et al* 1979; Jones *et al* 1979; Summerville *et al* 1979) have shown that the porphyrin ligand has a labilising effect on Cr(III) substitution reactions, making them 10^3 – 10^4 times faster than those with normal Cr(III) complexes. This labilisation has been attributed to strong mixing (π -bonding) of the chromium d_{yz} , d_{zx} orbitals and the lowest unfilled porphyrin π^* -orbitals, causing the metal to lose its d^3 character with the empty $d_{x^2-y^2}$, d_{z^2} orbitals being available for σ -bonding with axial ligands and the porphyrin macrocycle.

Considerable interest has centred on the effect of axial ligation. Summerville *et al* (1977), showed that changes in axial ligation of the heme moiety in natural heme proteins causes changes in the biological role of the heme protein.

It has also been pointed out (Inhoffen *et al* 1968) that the properties of a metallo protein are influenced by the geometry, charge, electronegativity, degree of σ - and π -bonding of the metal porphyrin systems and the degree of σ - and π -bonding of the metal-axial ligand system.

While a number of publications have reported electrochemical studies on porphyrin

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1984), studies on axial ligation of metalloporphyrins by pyridyl groups has been limited, especially for Cr(III) tetraphenylporphyrin complexes, such as Cr(III)-(TPP)Cl. Bottomley and Kadish (1981) and Larkworthy (1984) suggest, on the basis of electrochemical investigations, that two discrete pathways for electron transfer are possible in the reduction of Cr(TPP)Cl(L), where TPP = tetraphenylporphyrin, L = substituted pyridine.

To investigate the possible inductive and steric factors associated with axial ligation of Cr(III) (TPP)Cl by different substituted pyridine ligands, the electrochemical behaviour of the complexes formed with pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline has been determined and the relationship between reduction potentials, the electronic band I transition and the binding energy of the $2p_{3/2}$ level examined.

Experimental

Electrochemical data (DC cyclic voltammetry, CV, and DC polarography, DCP) were recorded on an AMEL 471 Multipolarograph, 3-electrode system. The reference, auxiliary and working electrodes were the saturated calomel electrode (SCE), platinum wire electrode and either a hanging mercury drop electrode (HMDE) (CV) or a dropping mercury electrode (DME) (DCP), respectively. All solutions were of concentration 1.5×10^{-3} M, with 0.2 M tetrabutylammonium perchlorate as supporting electrolyte together with 50 μ l of 0.1 % Triton-X100 surface active agent. The solvent for cyclic voltammetry was either acetonitrile or dimethylsulphoxide. The latter solvent was used exclusively for DC polarography.

X-ray photoelectron spectra were recorded on a spectrometer previously described by Kemeny *et al* (1973), using AlK α photons of 1486.6 eV energy. The powdered samples were adhered to a copper sample holder with double-sided adhesive tape. All core level binding energies (E_f) were calibrated relative to the Cu $2p_{3/2}$ core level binding energy (932.5 eV) of the reversible copper sample holder, relative to the spectrometer Fermi Level, in accordance with the procedure of Barr (1978). The copper metal surface was scraped and passivated in air for 1–2 min prior to subjection to a vacuum reaching 10^{-7} HPa (torr) in approximately 20 min. Determination of surface charging effects was made by the standard method (Kohiki *et al* 1983), which involves variation of the intensity of the AlK α x-rays (50–300 W, Leybold-Heraeus RQ 10/63 x-ray source). No surface charging effects were detected which suggests that the generation of secondary electrons inside the spectrometer housing was sufficient to act as a 'flood-gun' for the sample surface. As a result, no correction for a 'floating' Fermi level was necessary in calibrating core level binding energies. The associated error with this is (± 0.3 eV).

Ultraviolet and visible spectra were recorded on a Shimadzu, UV-240 Recording Spectrophotometer using 1 cm matched quartz cells and purified chloroform as solvent.

Chemicals: TPPH $_2$; this was purified according to the procedure of Datta-Gupta and Williams (1971);

Elemental analysis: Found: C, 58.76; H, 3.72; N, 7.00%; Calcd.: (as $\text{CrCl}_4/1.33/1.5 \text{ CrCl}_3 \cdot 1.5\text{HCl}_3$) C, 58.72; H, 3.72; N, 7.00%.

The $\text{Cr}(\text{TPP})\text{ClL}$ adducts, where L = pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline, were prepared according to the following general procedure.

The heterocyclic ligand, L , was added in excess (10 cm^3) to a solution of $\text{Cr}(\text{TPP})\text{Cl}$ (0.5 g) dissolved in purified chloroform (50 cm^3) and stirred at ambient temperature for 3 hours. Slow evaporation of the solvent afforded the $\text{Cr}(\text{TPP})\text{Cl}(L)$ adducts, with an average yield of 95% after washing with anhydrous, purified chloroform. The 4-cyanopyridine adduct was prepared by adding 4-cyanopyridine (9.5 g) in benzene (30 cm^3) to $\text{Cr}(\text{TPP})\text{Cl}$ (0.5 g) in chloroform (50 cm^3), followed by slow evaporation of the solvents.

The elemental analysis for the $\text{Cr}(\text{TPP})\text{Cl}(\text{Pyridine})$ adduct is as follows: Found: C, 75.50; H, 4.20; N, 9.00%; Calcd.: C, 75.52; H, 4.27; N, 8.98%.

3. Results and discussion

Electrochemical data for the $\text{Cr}(\text{TPP})\text{Cl}$ adducts with the following axial ligands—pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline are shown in table 1, along with electrochemical data for selected chromium porphyrins extracted from the literature for comparative purposes. The xps E_b^f ($\text{Cr } 2p_{3/2}$) binding energies and near infrared Band I [$a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow e_g(\pi^*)$] electronic transitions are recorded in table 2.

Elemental analyses yielded results which indicated that the (*meso*-tetraphenylporphyrin)chromium(III) chloride dissolved in dimethylformamide had the formula $\text{Cr}(\text{TPP})\text{Cl}(\text{DMF})$. However, in the formation of the pyridyl and morpholyl adducts, a dissociative exchange mechanism: $\text{Cr}(\text{TPP})\text{Cl}(\text{DMF}) + L \rightleftharpoons \text{Cr}(\text{TPP})\text{Cl}(L) + \text{DMF}$ takes place, where L = an axial base ligand.

To distinguish between metal and ligand redox reactions in metalloporphyrins, Furrhop (1974) and Felton (1979) established the general pattern that the numerical difference between the half-wave potentials of the first ligand oxidation ($E_{1/2}^{\text{ox}}$) in nitrile solvents and the first ligand reduction in DMSO ($E_{1/2}^{\text{red}}$), i.e., $\Delta E_{1/2}^{\text{ox/red}} = \delta$, equals $2.25 \pm 0.15 \text{ V}$, when the redox processes involve the porphinato moiety and not the metal. Further criteria are that the normal difference between the 1st and 2nd ring oxidations, $\Delta_{\text{ox}} = E_{1/2}^{\text{ox}}(2) - E_{1/2}^{\text{ox}}(1)$ equals $0.29 \pm 0.05 \text{ V}$, while the normal difference between the 1st and 2nd ring reductions $\Delta_{\text{red}} = E_{1/2}^{\text{red}}(1) - E_{1/2}^{\text{red}}(2)$ should lie in the range $0.49 \pm 0.08 \text{ V}$.

From the literature data cited in table 1 for chromium-porphyrin complexes, it is clear that, in general, these complexes exhibit Δ_{ox} and Δ_{red} values within the normally accepted ranges. Further, it would appear that they are, to certain extents, subject to solvation effects and varying inductive and steric effects by the axial ligand groups. Further, the similarity of δ for TPPH_2 and $\text{Cr}(\text{TPP})\text{Cl}$ would tend to support the view that there is negligible mixing of the ligand (a_{2u} , a_{1u}) and metal $e_g(d\pi)$ molecular orbitals, as metallation does not significantly affect the value of δ .

Table 1. Electrochemical data for selected chromium porphyrins and TPPH₂ free base.

Complex	CV oxidation (CH ₃ ON)			CV reduction (DMSO)			DCP reduction (DMSO)		
	Ligand		Metal	Ligand		Metal	Ligand		Metal
	<i>E</i> _{1/2} (2) (v)	<i>E</i> _{1/2} (3) (V)	III → IV (V)	<i>E</i> _{1/2} (2) (V)	<i>E</i> _{1/2} (3) (V)	III → II (V)	<i>E</i> _{1/2} values (V)	<i>E</i> _{1/2} (V)	III → II (V)
Cr(TPP)-Cl(DMF)	+1.20	+1.42	+0.53	0.22	-1.27	-0.75	0.43	2.47	-0.06 -0.37
Cr(TPP)-Cl(Py)	+1.01	+1.20	+0.33	0.19	-1.53	-0.80	—	—	-0.1 -0.37 -0.55
Cr(TPP)-Cl(2-Pic)	+1.06	—	+0.25	—	-1.65	-0.42	0.43	2.28	-0.05 -0.38 -0.56
Cr(TPP)-Cl(2,6-lut)	+1.01	—	—	—	-1.31	-0.43	—	2.32	-0.09 -0.25 -0.40
Cr(TPP)-Cl(4-CyPy)	+0.98	—	—	—	-1.25	-1.37	0.12	2.23	-0.02 -0.36 -0.50
Cr(TPP)-Cl(Mor)	+1.16	—	—	—	-1.24	-0.96	—	2.40	-0.03 -0.47
Cr(TPP)-Cl(4-Pic)	+1.08	—	—	—	-0.91	-0.73	0.28	1.99	-0.06 —
TPPH ₂ ^a	+1.12	+0.97	—	0.15	—	—	—	—	—
TPPH ₂ ^b	+1.28	+0.95	—	0.33	-1.05	—	0.42	2.33	—
Cr(OEP) ^c (OH) in CH ₂ Cl ₂	+1.22	+0.99	+0.79	0.23	-1.35	-1.14	—	2.57	—
Cr(OEP) ^d (OH) in DMSO	+1.22	+0.99	+0.79	0.23	-1.34	-1.13	—	2.56	—
Cr(TPP) ^e -ClO ₄ in CH ₂ Cl ₂	+1.39	+1.03	—	0.36	-0.81	—	0.39	2.20	—
Cr(TPP) ^e (NO) in CH ₂ Cl ₂	—	—	—	—	-1.86	—	1.05	—	—
[Cr(TPP) ^e -Cl(Py) ₂] ⁺ in CH ₂ Cl ₂	+1.22	+0.95	—	—	—	—	—	—	—
Cr(TPP) ^e -Cl(Py) in CH ₂ Cl ₂	—	—	—	—	—	-0.75	—	—	—
Cr(TPP) ^e -Cl in CH ₂ Cl ₂	+1.29	+0.87	—	—	—	-1.07	—	—	—
Cr(TPP) ^d -in butyronitrile	—	—	—	0.42	-1.01	—	0.19	2.30	—
Cr(TPP) ^d -Cl in CH ₂ Cl ₂	+1.25	+0.87	+0.79	0.38	-1.06	—	0.63	—	—
Cr(TPP) ^b -Cl	—	—	+0.79	—	-1.69	-1.06	—	—	—

^a Fuhrhop (1974); ^b Felton (1979); ^c Fuhrhop *et al* (1973); ^d Newton and Davis (1975); ^e Kelly and Kadish (1984).

Abbreviations: DMF = dimethylformamide; DMSO = dimethylsulphoxide; OEP = octaethylporphyrin; Py = pyridine; 2-Pic = 2-picoline; 2,6-lut = 2,6-lutidine; 4,6-CyPy = 4-cyanopyridine; Mor = morpholine; 4-Pic = 4-picoline.

No.	Complex	XPS* E_f (Cr $2p_{3/2}$) (eV)	UV-vis* band I	$/E_{1/2}^{\text{red}}$ (III-II)/(V)*
			($a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow e_g(\pi^*)$) (nm)	
1	Cr(TPP)Cl(DMF)	570.8	810.0	-0.75
2	Cr(TPP)Cl(Py)	572.2	788.0	-0.83
3	Cr(TPP)Cl(2-Pic)	571.5	809.5	-0.56
4	Cr(TPP)Cl(4-Pic)	569.1	830.0	-0.46
5	Cr(TPP)Cl(2,6-lut)	569.9	811.0	-1.09
6	Cr(TPP)Cl(4-CyPy)	571.6	795	-0.91
7	Cr(TPP)Cl(Mor)	573.3	806	-0.68

* Errors: XPS (± 0.3 eV); band I (± 1.0 nm); $/E_{1/2}^{\text{red}}$ (III-II)/(± 0.05 V); abbreviations: refer table 1, foot note.

As representatives of the voltammograms obtained for the reduction of the different Cr(TPP)·Cl·L adducts, those for the morpholine (Mor) and pyridine (Py) adducts are shown in figures 1 and 2, respectively. From the voltammograms, the values of δ and Δ_{red} were obtained. For the oxidation of the adducts in acetonitrile, the values of δ and Δ_{ox} were also obtained. All values are listed in table 1, which in addition contains the DC polarographic data in DMSO for Cr(TPP)Cl·DMF and the six adducts of Cr(TPP)Cl.

In the polarographic reduction of the adducts, 4 polarographic waves were, in general, detected. The half-wave potentials of these waves were found to be in the range (1) -0.06 to -0.1; (2) -0.25 to -0.47; (3) -0.4 to -0.56 and (4) -0.50 to -0.86. Of the four waves obtained in the polarographic investigations, the fourth was found to be dependent on the metal concentration and gave a value of $n \cong 1$ for the number of electrons transferred. It thus relates to the reduction $\text{Cr(III)} \rightleftharpoons \text{Cr(II)}$. The variation of $E_{1/2}$ for the different adducts reflects the inductive, steric and solvent effects associated with different adducts.

In cyclic voltammetry, as seen from figure 1 for the reduction of the adduct

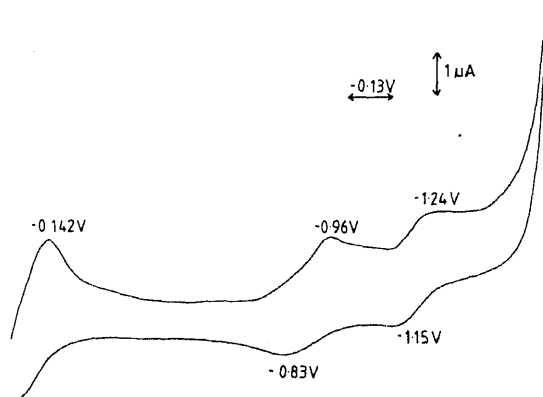


Figure 1. Cyclic voltammogram at HMDE for reduction of Cr(TPP)Cl·Mor adduct. (0 to -1.55 v; scan rate 0.050 v/s; $T = 25^\circ\text{C}$) in DMSO; 0.2 M But₄NClO₄; 50 μl 0.1 % TRX 100.

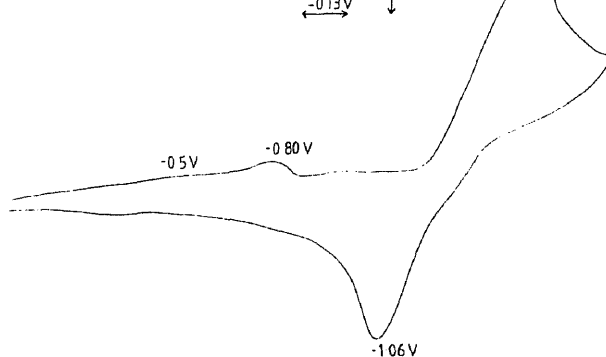


Figure 2. Cyclic voltammogram at HMDE for reduction of $\text{Cr}(\text{TPP})\text{Cl} \cdot \text{Py}$ adduct (0 to -1.17 V; scan rate 0.050 V/s; $T = 25^\circ\text{C}$) in DMSO; 0.2 M $\text{But}_4\text{NClO}_4$; 20 μl 0.1% TRX 100.

$\text{Cr}(\text{TPP})\text{Cl} \cdot \text{Mor}$ in DMSO, three peaks were found on the cathodic sweep: (1) -0.142 V; (2) -0.96 V; (3) -1.24 V. The peak at -0.96 V was found to be dependent on the concentration of Cr(III) and thus represents the reduction $\text{Cr}(\text{III}) \rightleftharpoons \text{Cr}(\text{II})$. The peak at -1.24 V does not show the characteristics of an adsorption wave and is not associated with the reduction of the metal. It is, therefore, assigned as a ligand peak. The anodic sweep shows a peak at -1.15 V which corresponds to the cathodic peak at -1.24 V. The peak at -0.142 V appears to be an adsorption wave.

The results obtained with the six adducts (table 1) show accord with the criteria mentioned above and indicate that the system behaves as a normal metalloporphyrin. The variations of δ - and Δ_{red} for the adducts are mainly attributed to different inductive effects from the heterocyclic axial groups. The value of δ reflects the 2.18 eV difference between the e_g and $(a_{1u}), (a_{2u})$ molecular orbitals of the porphinato ligand.

It appeared from this work that the mean half-wave potential for the reduction of the chromium(III) ion has some relationship to the size of the electronic band I ($a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$) transition. To examine this, the experimental value for the electronic band I transition for each adduct was determined and plotted against the corresponding $E_{1/2}$ value. The result is shown in figure 3. The results indicate a direct relationship between electronic band I transition and $E_{1/2}$ with both dependent on the axial ligand. This may be due to changes in the electron withdrawing ability of the chromium ion on the porphinato ring nitrogen atoms, as a direct consequence of changing axial ligands. The deviation of the 2,6-butidine adduct from the line in figure 3 is interesting and may be due to both an axial ligand inductive effect on the chromium ion and steric hindrance between the 2,6-dimethyl groups on the ligand and the porphinato nitrogen atoms.

An approach that may be used to examine the electron density on the chromium as the axial ligand is changed is by means of XPS. Consequently, the value of $E_b^f(\text{Cr } 2p_{3/2})$ was determined by XPS for each $\text{Cr}(\text{TPP})\text{Cl} \cdot L$ adduct and the value obtained plotted against the corresponding $E_{1/2}^{\text{red}}(\text{III-II})$ value. Results are shown in figure 4 and reflect a small increase in the $(\text{Cr } 2p_{3/2})$ binding energy and a small increase in $E_{1/2}$ values with changing axial ligands. It is interesting to note that, in figures 3 and 4, it is the 2,6-butidine ligand which shows a marked deviation from the straight line. It is supposed

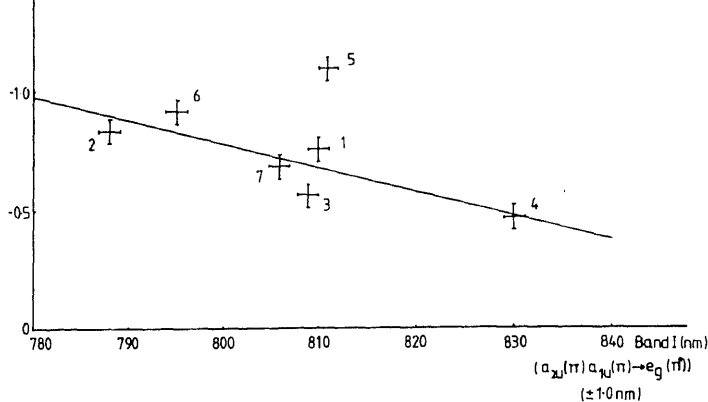


Figure 3. Correlation of $E_{1/2}$ values and the corresponding electronic Band I transitions for the (meso-tetraphenylporphyrin)chromium(III) adducts.

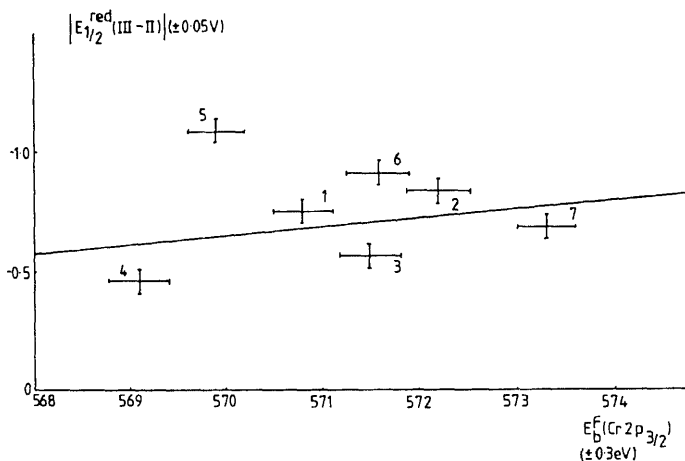


Figure 4. Correlation of $E_{1/2}$ values and the corresponding $E_b^F(\text{Cr } 2p_{3/2})$ binding energies for the (meso-tetraphenylporphyrin)chromium(III) adducts.

that the reason for this is that it is reflecting a significant steric interaction of this axial ligand with the porphinato nitrogen atoms. This is confirmed (figure 4) by the large E_b^F range (569–573.5 eV) caused by the steric and inductive influences on the Cr $2p$ orbitals.

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Preparation and characterisation of phosphate and arsenate apatites of barium and their solid solution

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Abstract. Phosphate and arsenate apatites of barium and one of their solid solutions were prepared by a wet method and characterized by chemical, x-ray, infrared and thermogravimetric analyses. Chemical analysis gave the stoichiometry of the samples while x-ray and infrared studies confirmed the formation of a solid solution. The range of thermal stabilities of the samples was established through thermogravimetric analysis.

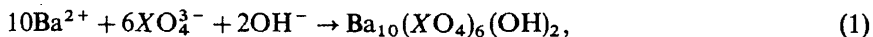
Keywords. Apatites; solid solutions; thermogravimetric analysis.

1. Introduction

Calcium hydroxylapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, the principal inorganic constituent of bones and teeth (Posner 1961) undergoes several cationic and anionic exchange reactions leading to the formation of the corresponding isomorphs. Phosphate and arsenate apatites of barium (abbreviated as BaPA and BaAsA respectively) are important consequent upon the toxicity of elemental barium (Boyd 1962; Deichmann and Gerarde 1962) and arsenic (Stewart and Stolman 1960). The need for a wet method for preparation of BaPA, BaAsA and a representative solid solution was felt since the earlier methods (Narasaraju *et al* 1975; Mayer *et al* 1979) failed and hence the present investigations adopting co-precipitation were undertaken. In addition, the samples were characterized through chemical, x-ray IR and thermogravimetric analyses.

2. Experimental

The samples were prepared by a modification of an existing method (Narasaraju *et al* 1977) used for other apatites and was based on the equation,



where $X = \text{P}$ or As or $(\text{P} + \text{As})$.

While stock solutions ($\approx 0.5 \text{ M}$) of barium acetate, diammonium hydrogen phosphate were prepared in CO_2 -free water, sodium arsenate solution was obtained by dissolving As_2O_5 in sodium hydroxide solution. Barium, phosphorus and arsenic contents of the respective solutions were determined by complexometric (West 1969),

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methods, respectively. Appropriate volumes of these solutions based on the stoichiometry given in (1), required for ≈ 30 g yield of the desired sample were mixed at 37°C with the required volume of ethylene-diamine to attain a pH of 12. CO_2 -free air was bubbled through the mixture to eliminate the formation of carbonate apatite and to keep it well stirred. The suspension was refluxed for about 3 hr, left overnight and washed till the washings were neutral. The precipitate, suspended in a 2% EDTA solution containing ammonium chloride and ammonium hydroxide (Wier *et al* 1971; Smith *et al* 1974) to maintain a pH of 10, was subjected to rigorous mechanical shaking for about 6 hr. It was filtered through a G_4 sintered glass crucible and washed with double distilled water till the washings were neutral and free from EDTA. A 2% portion of each of the samples was washed with acetone and air-dried, while the rest of the sample was dried to constant weight at 110°C , cooled in a desiccator and analysed (Vogel 1962), for PO_4^{3-} , AsO_4^{3-} and Ba^{2+} . X-ray diffraction patterns of the samples were recorded using CuK_α radiation. The IR absorption spectra in the range, $650\text{--}4000\text{ cm}^{-1}$, were recorded as nujol mulls with a Perkin Elmer IR spectrometer (Model 297) equipped with potassium bromide optics. The densities of the samples were determined by standard methods (Salzberg *et al* 1966). The acetone-washed and air-dried samples were subjected to thermoanalytical investigations using a thermogravimetric furnace (Fertilizer Corporation of India, Sindri, India), upto 800°C .

4. Results and discussion

Chemical analyses gave atomic ratios, $\text{Ba}/(\text{P} + \text{As})$, ranging between 1.66 to 1.68, which are in good agreement with the stoichiometric value, 1.67 (see table 1) indicating the suitability of the methods adopted for the preparation and chemical analyses of the samples.

The lattice parameters a and c were found to be 10.14 and 7.73 Å for BaPA, and 10.66 and 7.92 Å for BaAsA, while the solid solution has intermediate values. A linear dependence of the unit cell volumes of the samples on their arsenate content shows the validity of Vegard's law confirming thereby the homogeneity of the samples. A marginal dilation in the unit cell volumes and hence, the molar volumes of the samples consequent upon the replacement of PO_4^{3-} by AsO_4^{3-} (covalent radii 1.10 and 1.18 Å, respectively, Wells 1950), was observed as expected (see table 2). This is in accordance with the criteria of formation of solid solutions (Azaroff 1960).

The IR traces (Mayer *et al* 1979) of the solid solution of BaPA and BaAsA exhibited predominant absorption peaks due to PO_4^{3-} , ASO_4^{3-} and OH^- while the end members showed the characteristic peaks of PO_4^{3-} or AsO_4^{3-} along with that of OH^- . The weight loss in each case was found to be uniform upto 500°C beyond which there was the weight became constant. These studies indicated that the samples were thermally stable upto the temperature investigated. In case thermal decomposition is to set in within this range, a discontinuity in the plot depicting weight loss as a function of temperature is anticipated. The uniform weight loss observed as a function of temperature can be attributed to the loss of adsorbed water. The presence of adsorbed water (Rootare *et al* 1962; Chickerur *et al* 1969) in the samples of apatites prepared by these wet methods can be explained on the basis of the large surface area associated with them consequent upon their small particle size.

Table 1. Chemical analyses of phosphate and arsenate apatites of barium and a representative solid solution of the two.

Samples	Weight (%) [*]						g atom ratio Ba/(P + As)	Molecular formula [†]
	Ba		P		As			
	Found	Calculated	Found	Calculated	Found	Calculated		
	Found	Calculated	Found	Calculated	Found	Calculated		
BaPA	69.69	69.46	9.42	9.40	—	—	1.67	Ba ₁₀ (PO ₄) ₆ (OH) ₂
Solid solution	65.05	65.12	4.38	4.41	10.72	10.66	1.66	Ba ₁₀ (PO ₄) ₃ (AsO ₄) ₃ (OH) ₂
BaAsA	60.86	61.29	—	—	19.75	20.06	1.68	Ba ₁₀ (AsO ₄) ₆ (OH) ₂

^{*} Mean of six determinations; [†] based exclusively on Ba, P and As contents, (OH⁻) content being assumed stoichiometric.

Sample	Lattice parameters A		Molar volume ml/mole		IR data Wave number (cm ⁻¹)		
	a	c	$V_{uc} \cdot N$	M/d	PO ₄ ³⁻	AsO ₄ ³⁻	OH ⁻
BaPA	10.14	7.73	414	413	990	—	3560
Solid solution	10.38	7.91	444	469	980	800, 870	3560
BaAsA	10.66	7.92	469	502	—	800, 870	3560

Acknowledgement

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Kinetics of oxidation of fluorene by alkaline hexacyanoferrate(III)

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Abstract. The kinetics of oxidation of fluorene by alkaline hexacyanoferrate(III) is followed under pseudo-first-order conditions in 50% aqueous acetonitrile. The reaction is first-order both in the oxidant and substrate. The rate dependence on $[\text{NaOH}]$ is unity. Hexacyanoferrate(II) retards the reaction. The product of oxidation is fluorenone and the stoichiometry between the substrate and the oxidation is 1:4. A large positive salt effect and specific cation effect are observed. A tentative mechanism accounting for all the observations is envisaged.

Keywords. Fluorene; oxidation; hexacyanoferrate(III); kinetics.

1. Introduction

Even though hexacyanoferrate(III) is a weak oxidant, a number of organic substrates were oxidised by it under proper conditions and the kinetics of these reactions were rigorously investigated by several workers (Speakman and Waters 1955; Mahapatra and Radhakrishnamurti 1976b; Hamilton and McDonald 1973; Chatterji *et al* 1976). In all these cases the important step is conceived to be the abstraction of an electron by the one-electron oxidant hexacyanoferrate(III) (Thyagarajan 1958; Wilson 1966). Sluggish oxidation reactions were found to be catalyzed by metal ions like Os(VIII) (Singh *et al* 1975, 1977b; Radhakrishnamurti 1979), Ru(III) (Singh and Singh 1978; Radhakrishnamurti and Sahu 1979a, b) and Cu(II) (Bridgart *et al* 1973a, b; Mathur and Srivastava 1977; Bansal and Singh 1979). A unique instance of the oxidation of an alkyl function, activated by a nitro group, with alkaline hexacyanoferrate(III) was reported recently by Mahapatra and Radhakrishnamurti (1976b). This prompted us to take up the study of the oxidation of fluorene (Fl), which contains a reactive methylene function at the 9-position. The literature survey revealed that the kinetics of the oxidation of fluorenes by hypobromite (Kozuka *et al* 1975), ceric ammonium nitrate (Narasimhan and Venkatasubramanian 1977a), phenyliodosyl acetate (Panda and Radhakrishnamurti 1979), lead tetraacetate and V(V) (Mahapatra and Radhakrishnamurti 1976a; Narasimhan and Venkatasubramanian 1979b) only have been studied. The present investigation deals with the oxidation of fluorene by alkaline hexacyanoferrate(III) under different conditions. As far as we know this is the first report of the oxidation of an aromatic hydrocarbon by alkaline hexacyanoferrate(III). However, recently there is a report on the oxidation of naphthalene by hexacyanoferrate(III) in acetic acid-perchloric acid medium (Bhattacharjee and Mahanti 1983).

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Potassium hexacyanoferrate(III), sodium hydroxide, potassium chloride, sodium chloride and potassium hexacyanoferrate(II) were of AnalaR grade and used as received. Technical grade fluorene (Koch-Light) was purified by chromatography followed by crystallization from ethanol (m.p. 113°). Acetonitrile was distilled before use. Carbon dioxide-free sodium hydroxide solution was prepared by the standard procedure (Vogel 1961). Double distilled water was used throughout for preparing reaction mixtures. The kinetic studies were carried out in 50% aqueous acetonitrile under pseudo-first-order conditions with hexacyanoferrate(III) as the limiting reagent. The progress of the reaction was followed by estimating the unreacted hexacyanoferrate(III) iodometrically. For reasons of maintaining considerably high ionic strength of the reaction medium low concentrations of sodium hydroxide, fluorene and hexacyanoferrate(III) (5×10^{-4} M) had to be used allowing greater solubility of potassium chloride. In such cases the spectrophotometric method was adopted using a Carl-Zeiss Specord uv-vis Spectrophotometer. Equal volumes of solutions of appropriate concentrations of the reactants were mixed after allowing them to attain equilibrium temperature in a constant temperature water bath ($\pm 0.1^\circ$). The reaction was conducted in a vessel wrapped with black cloth. Since hexacyanoferrate(III) is the limiting reagent the rate, v , is given by

$$v = k_{\text{obs}} [\text{Fe}(\text{CN})_6^{3-}]$$

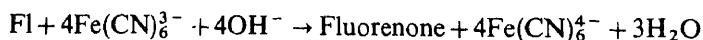
where k_{obs} is the observed pseudo-first-order rate constant obtained as the slope of a line resulting from a plot of log of the volume of the titrant versus time. The slopes for all the runs were obtained by the method of least squares and the correlation coefficients for all the runs were excellent. All the runs were carried out after removing air by passing nitrogen through solutions of the reactants before mixing.

2.1 Product analysis

The reaction mixture was analyzed to identify the product after keeping it for two days for completion. The acetonitrile was removed and the aqueous layer extracted with benzene. The benzene layer was dried with anhydrous magnesium sulphate. The residue obtained after the evaporation of benzene was subjected to column chromatography using alumina. Petroleum ether and petroleum ether-benzene eluates gave unreacted fluorene. The benzene eluate yielded a yellow compound which melted at 80–81° after crystallization from petroleum ether. It was confirmed to be fluorenone by determining the mixed melting point with an authentic sample of fluorenone and by spectroscopic analysis.

2.2 Stoichiometry

The stoichiometry of the reaction was determined by allowing an excess of hexacyanoferrate(III) to react with fluorene under alkaline conditions and estimating the unreacted hexacyanoferrate(III) in an acid condition after the completion of the reaction. The stoichiometry of the reaction was 1 : 4 between the substrate and oxidant. The expected stoichiometry for the fluorenone formation is the same as above



3.1 Effect of varying [fluorene]

The order of the reaction with respect to fluorene was determined by varying [F1] and keeping other experimental variables constant. The results are presented in table 1. The pseudo-first-order rate constants vary proportionally with the initial [F1]. The second-order rate constants k_2 ($k_2 = k_{\text{obs}}/[\text{F1}]$) remain constant for all the runs performed. This confirms the unit dependence of the rate of oxidation on [F1].

3.2 Effect of varying [hexacyanoferrate(III)]

The reaction is first order in hexacyanoferrate(III) as shown by the good correlation ($r = 0.994$) for the plot of log of concentration of hexacyanoferrate(III) versus time for 70% completion of the reaction. But, contrary to the expectation, the k_{obs} value changes with the change in the initial concentration of hexacyanoferrate(III) (table 2). Though for any one kinetic run there is a first-order dependence on hexacyanoferrate(III), the rate decreases with the increase in the initial concentration of hexacyanoferrate(III). Such an observation is not uncommon and many workers have come across the anomalous behaviour in the different oxidation studies (Hinshelwood and Shorter 1950; Kansal *et al* 1979; Bakore *et al* 1971; Bhagawat and Yadav 1964; Acharya *et al* 1976; Venkatasubramanian and Srinivasan 1970; Krishna Pillay and

Table 1. Effect of [F1].

[F1] $\times 10^3$ (M)	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$k_2 \times 10^2$ ($\text{l mol}^{-1} \text{sec}^{-1}$)
7.0	1.84	2.62
8.0	2.07	2.59
9.0	2.27	2.52
10.0	2.52	2.52

$[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} \text{ M}$; $[\text{NaOH}] = 2 \times 10^{-1} \text{ M}$;
 $[\text{KCl}] = 2.5 \times 10^{-2} \text{ M}$; solvent = 50% aqueous CH_3CN ;
 temperature = 35° .

Table 2. Effect of $[\text{K}_3\text{Fe}(\text{CN})_6]$.

$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^4$ (M)	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$k_2 \times 10^2$ ($\text{l mol}^{-1} \text{sec}^{-1}$)
2.5	4.78	4.78
5.0	3.85	3.85
7.5	3.39	3.39
10.0	2.52	2.52

$[\text{F1}] = 1 \times 10^{-2} \text{ M}$; $[\text{NaOH}] = 2 \times 10^{-1} \text{ M}$; $[\text{KCl}] = 2.5 \times 10^{-2} \text{ M}$; solvent = 50% aqueous CH_3CN ; temperature = 35° .

3.3 Effect of varying [sodium hydroxide]

The reaction is base-catalyzed as shown by the results in table 3. A plot of log pseudo-first-order rate constants against $[\text{NaOH}]$ gives a straight line ($r = 0.999$) with slope = 1.29. This indicates the first-order dependence of the rate on sodium hydroxide concentration.

3.4 Effect of ionic strength

With the concentrations of the oxidant, substrate and sodium hydroxide given in table 4, we have been unable to vary the concentration of potassium chloride very widely for practical reasons. Small changes in ionic strength did not have much influence on the rate of the reaction as shown in table 4. To have wide variation in the concentration of potassium chloride, the concentrations of other components were greatly decreased and the change of concentration of hexacyanoferrate(III) was followed spectrophotometrically. The results (table 5) show that the pseudo-first-order rate constant increases with increasing ionic strength indicating a positive salt effect. The reaction was found to show specific cation catalysis. For example, for the same

Table 3. Effect of $[\text{NaOH}]$.

$[\text{NaOH}] \times 10$ (M)	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$k' \times 10^4 = k_{\text{obs}}/[\text{NaOH}]$ ($\text{l mol}^{-1} \text{sec}^{-1}$)
0.50	0.61	1.22
1.25	1.60	1.28
1.75	2.28	1.30
2.00	2.52	1.26

$[\text{Fl}] = 1 \times 10^{-2} \text{ M}$; $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} \text{ M}$; $[\text{KCl}] = 2.5 \times 10^{-2} \text{ M}$; solvent = 50% aqueous CH_3CN ; temperature 35° .

Table 4. Effect of $[\text{KCl}]$.

$[\text{KCl}] \times 10^2$ (M)	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$k_2 \times 10^2$ ($\text{l mol}^{-1} \text{sec}^{-1}$)
0.00	2.50	2.50
1.25	2.61	2.61
2.50	2.52	2.52
5.00	2.47	2.47
7.50	2.49	2.49

$[\text{Fl}] = 1 \times 10^{-2} \text{ M}$; $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} \text{ M}$;
 $[\text{NaOH}] = 2 \times 10^{-1} \text{ M}$; solvent = 50% aqueous
 CH_3CN ; temperature 35° .

0.0	2.55	0.51
2.0	3.95	0.79
3.0	8.42	1.68

[FI] = 5×10^{-3} M; $[K_3Fe(CN)_6] = 5 \times 10^{-4}$ M;
 [NaOH] = 5×10^{-2} M; solvent = 50% aqueous
 CH₃CN; temperature = 35°.

Table 6. Effect of $[K_4Fe(CN)_6]$.

$[K_4Fe(CN)_6] \times 10^3$ (M)	$[KCl] \times 10$ (M)	$k_{obs} \times 10^5$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
0.0	3.00	8.42	1.68
0.5	2.98	5.67	1.13
1.0	2.96	5.35	1.07
5.0	2.80	4.64	0.93

[FI] = 5×10^{-3} M; $[K_3Fe(CN)_6] = 5 \times 10^{-4}$ M; [NaOH] = 5×10^{-2} M;
 solvent = 50% aqueous CH₃CN; temperature 35°.

concentration of K⁺ and Na⁺ (3×10^{-1} M) with the other variables constant, the k_2 values are 7.30×10^{-3} and 3.26×10^{-3} l mol⁻¹ sec⁻¹, respectively. The specific cation effect suggests the interaction to be between negatively charged ions (Olson and Simonson 1949).

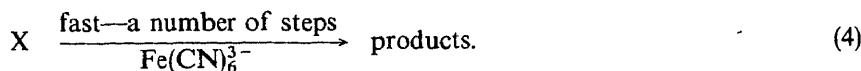
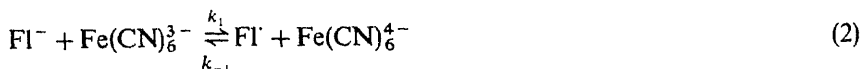
3.5 Effect of varying [hexacyanoferrate(II)]

The effect of change of [hexacyanoferrate(II)] on the rate of oxidation was studied under constant ionic strength by adjusting the concentration of potassium chloride suitably (see table 6). Addition of hexacyanoferrate(II) to the reaction mixture decreases the rate indicating that it is involved in an equilibrium step prior to the rate-limiting step.

4. Mechanism

The oxidation reaction is first-order both with respect to substrate and oxidant. The rate dependence on concentration of hydroxide is unity and the reaction is retarded by hexacyanoferrate(II). A positive salt effect and the specific cation effect indicate that negatively charged ions interact. Since a ketone (fluorenone) is the product of oxidation starting from a hydrocarbon containing a reactive methylene function (9-position of fluorene) we anticipated that the corresponding alcohol, *viz*, 9-fluorenol might be the intermediate. An authentic sample of 9-fluorenol was prepared and rate of oxidation was followed. The rate of oxidation of 9-fluorenol ($k_2 = 8.92 \times 10^{-3}$ l mol⁻¹ sec⁻¹)

similar observation is made in the oxidation of fluorene by hypobromite in which the product of oxidation is fluorenone whereas the intermediate is not found to be the alcohol (Kozuka *et al* 1975). A tentative mechanism which is compatible with the experimental observations is given below:



Since the hydrogen atoms of the 9-position are sufficiently acidic owing to the activation by the two coplanar phenyl rings a proton is abstracted from the 9-position by the hydroxide ion in an initial equilibrium step. From the resulting carbanion an electron is removed by hexacyanoferrate(III) in an equilibrium step leading to the formation of the 9-fluorenyl radical (step 2). This intermediate radical gets converted into an intermediate whose nature we are not able to identify from the available experimental data and observations. However, we are forced to believe step (2) to be reversible and step (3) to be the slow step in order to account for all the experimental facts. The step in which a free radical changes over to another free radical is assumed to be the rate-determining one in the oxidative coupling reaction of 2,3',4-trihydroxybenzophenone by alkaline hexacyanoferrate(III) (Hamilton and McDonald 1973). The intermediate X reacts to form fluorenone probably through a number of fast steps. The involvement of hexacyanoferrate(II) in a prior equilibrium explains its retardation effect. Acrylamide was found to increase the rate of reaction by one and half times. This indicates that a free radical is involved in a slow step. Moreover the first-order dependence on hexacyanoferrate(III) concentration also implies a free radical intermediate (Hamilton and McDonald 1973). According to the above mechanism the following expressions may be obtained

$$\text{rate} = k'_2 [\text{Fl}^\cdot]. \quad (5)$$

Applying steady-state approximation

$$k_1 [\text{Fl}^-] [\text{Fe}(\text{CN})_6^{3-}] = k_{-1} [\text{Fl}^\cdot] [\text{Fe}(\text{CN})_6^{4-}] + k'_2 [\text{Fl}^\cdot]$$

Therefore

$$[\text{Fl}^\cdot] = \frac{k_1 [\text{Fl}^-] [\text{Fe}(\text{CN})_6^{3-}]}{k_{-1} [\text{Fe}(\text{CN})_6^{4-}] + k'_2} \quad (6)$$

Substitution for $[\text{Fl}^-]$ from the equilibrium (1) and further substitution in (5) gives

$$\text{rate} = \frac{k_1 k'_2 K [\text{Fl}] [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}]}{[\text{H}_2\text{O}] k_{-1} [\text{Fe}(\text{CN})_6^{4-}] + k'_2} \quad (7)$$

This rate expression accounts for the experimental observations.

The oxidation of fluorene by alkaline hexacyanoferrate(III) gives fluorenone; it takes place *via* free radicals and not through 9-fluorenol.

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Anisochrony of O-methylene protons of ethyl ester functions and structural factors in the connected chiral entities

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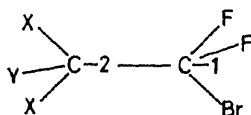
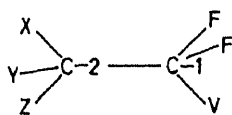
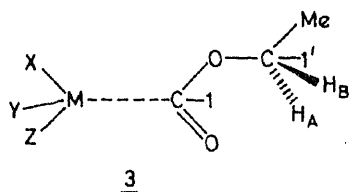
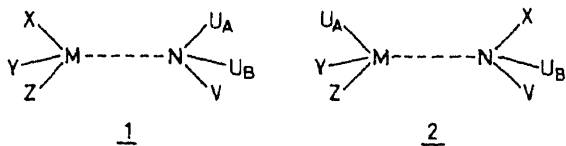
Abstract. (i) In *cis-trans* pairs of cyclic 1,3-dicarboxylic acid ethyl esters the *cis*-forms exhibit higher O-methylene proton (H_A , H_B) anisochrony than the *trans*-forms; (ii) anisochrony, easily observed in certain decalin-10-carboxylic ethyl esters, 'disappears' on one of the rings attaining the possibility of transforming into a 'twist' form; (iii) in certain pairs of chiral *sec*-ethyl esters and their *tert*-methylated analogues anisochrony is higher in the latter, contrary to expectation, while, in certain others, the reverse is observed. Attempted explanations are based on assessments whether H_A and H_B are or are not in highly different magnetic environments in conformers regarded as preferred. This subsumes the possibility that $XYZC-CO_2H_AH_BMe$ chiral ethyl acetates differ from $XYZC-CH_AH_BMe$ ethanes because intervention by the carboxyl group insulates the prochiral centre and allows anisotropic effects to gain somewhat in importance among mechanisms that discriminate between H_A and H_B so long as rotamer-population inequalities persist. Background information on why rotamer-population inequalities will always persist and on a heuristic that attempts to generalize the effects of XYZ in $XYZC-CU_AU_BV$ is provided. Possible effects when connectivity exists between a pair among X , Y , Z or when specific interactions occur between V and X , Y or Z are considered. An interpretation in terms of 'increasing conformational mobility' has been suggested for the observed increase in the rate of temperature-dependence of O-methylene anisochrony down a series of chiral ethyl esters.

Keywords. Anisochrony of geminal sensors; 'intrinsic' asymmetry (diastereotopism); gradient of anisotropy; Binsch heuristic; conformational analysis; internal conformation of ester groups; rotamerization of secondary and tertiary ester functions; H-bonding effects.

1. Anisochrony of geminal sensor units

Development of the understanding that anisochrony of geminal sensors, U_A , U_B , observed under conditions of rapid internal rotation in systems $XYZM-NU_AU_BV(1)$ has its origin in the same difference in topology as is immediately apparent in the case of the non-geminal ones in $YZU_AM-NU_BXV(2)$ has taken its time (Reisse *et al* 1978, hereafter denoted as ROBM). The purpose in recapturing parts of its history (for an early review, see Jennings 1975) is to highlight aspects relevant to ethyl ester functions connected to chiral entities (3) where 'chiral recognition' across the carboxy group confers nonequivalence on the O-methylene protons H_A , H_B .

The interpretation suggested by Drysdale and Philips (1957) for their observation with a series of 1,1-difluoroethanes (4a–d) took a course illustrative of the difficulties in conceptualizing the topological reasons for the anisochrony of geminal sensors. The finding was that even at 100°C the resonances of the geminal fluorines do not coalesce into a singlet (or into a single set) and the explanation offered was that rotation about the C–C bond is so hindered (to the point of restriction) as to locate the fluorines in non-equivalent environments. Since this explanation had the obvious implication that



4a: X = H ; Y = Ph ; Z = Br ; V = Br

b: X = H ; Y = Ph ; Z = Cl ; V = Cl

c: X = H ; Y = Cl ; Z = Br ; V = Br

d: X = F ; Y = Cl ; Z = Br ; V = Br

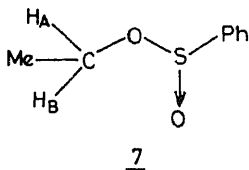
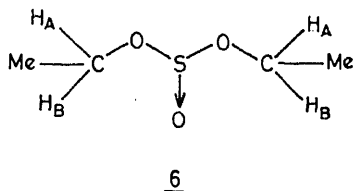
5a: X = Br ; Y = F

b: X = Cl ; Y = Br

c: X = Br ; Y = Ph

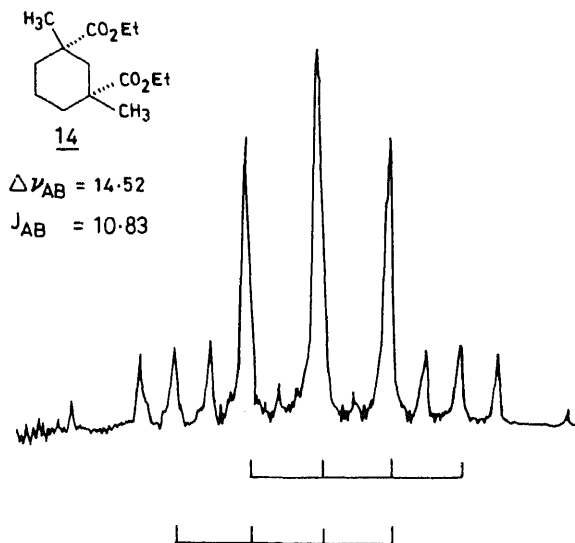
atropisomerism should be detectable in systems resembling 4a-d, Nair and Roberts (1957) sought evidence for the resolvability of systems like 5a-c in which hindrance was expected to be higher. They found that, while 1,2,2-tribromo-1,1,2-trifluoroethane (5a) continues to show 'normal' doublet CF₂ and triplet CF resonances down to -30°C, 1,2-dibromo-1,1-difluoro-2,2-dichloroethane (5b) freezes to an approximately 1.4:1 mixture of *meso*-(single line for the fluorines) and *dl*-(AB quartet for the fluorines) type rotamers when cooled to -80°C. These (and other related) observations were taken as indicating that, while it was indeed possible to freeze rotation when the temperature is brought down, rapid rotation must be presumed at the higher temperatures. In an attempt to resolve the apparent paradox in the ability to continue to observe a chemical shift difference between the geminal fluorines in 4a-d these authors suggested that 'unless the residence times of the molecule in each of the various rotational conformations are equal the resonances of geminal nuclei would show a difference in chemical shift'. It is difficult to see how rotation that is rapid enough to average the resonances of the various rotational conformations can allow the continued observability of chemical shift differences between geminal sensors arising from a difference in residence times.

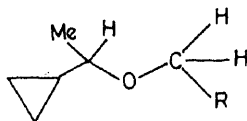
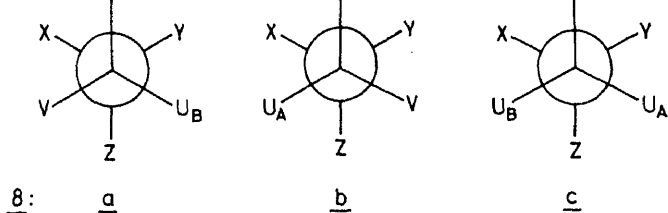
Finegold (1960a, b) reported observing two 1:3:3:1 quartets for the O-methylene protons of diethyl sulphite (6) and proceeded to suggest a difference in the nature of the two alkyl O-sulphite S bonds in order to explain what he took to be methylene-



methylene nonequivalence. Commenting on this, Waugh and Cotton (1961) pointed out that anisochrony arises in 6 from the symmetry nonequivalence of the H_A and H_B pairs (*cf.* Pople 1958) the effect of which cannot be destroyed even under conditions of rapid rotation. They cited the case of ethyl phenylsulphinate (7) in which the single O-methylene group gives rise not to a single 1:3:3:1 quartet but to an AB -system in which each line is split into a 1:3:3:1 quartet (for illustration see figure 1); the pattern in the case of 6 would have been similar had Finegold recorded its spectrum under conditions of better resolution since, under the reported conditions, the 'outer' quartets would have had not more than 2% of the total intensity of the 'inner' ones and would have been easily lost in noise.

Subsequent to this, the California group (Whitesides *et al* 1962) acknowledged that U_A and U_B in systems like 1 will be in distinct environments 'even assuming equal populations and rapid interconversion of the three conformers 8a, 8b and 8c' and added that "intrinsic asymmetry" of the methylene group [when $-CU_AU_BV = -CH_2CH_3$] might also be the cause of the observed nonequivalence'. Proceeding to look into the origins of the anisochrony—whether in conformer population difference or in 'intrinsic symmetry'—these authors replaced the methyl group of the ethyl





9a: R = Me

b: R = D

function in cyclopropylmethylcarbonyl ethyl ether (9a) by deuterium (to obtain 9b) and found that the nonequivalence of the methylene protons present in 9a 'disappears' on effecting the replacement. The result was interpreted as strongly suggesting that the nonequivalence springs from a conformational population difference since, the authors averred, replacement of the methyl by a deuterium would have acted towards equalizing the populations. This effort is now seen as having been misconceived since, as Gutowsky (1962) pointed out, only after demonstrating that such replacement is likely to cause the 'asymmetry effect' can one independently assert that its absence, in a given case, be taken as indicating that conformer population imbalance is the cause of the nonequivalence. This is virtually impossible since any replacement would alter the electrical and magnetic screening parameters of the original situation (it has been likened to 'throwing the child out with the bath water'; Franzen and Binsch 1973) and hence the chiral contribution to the anisotropy of the environment of the sensors; Stiles (1977) has examined from a theoretical standpoint the factors that make for the survival of chiral contributions under conditions of rapid rotation.

Gutowsky (1962) developed an equation which expresses the nonequivalence of the sensors U_A , U_B , measured under conditions after the individual spectra of entities such as 8a, 8b and 8c have attained coalescence (i.e. have been time-averaged by, for instance, raising the temperature), as a sum of population-dependent and -independent components. It can be written as (Raban 1966):

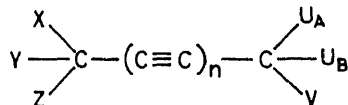
$$\Delta v_{\text{total}} = \sum_i^n (\chi_i - 1/n) \Delta v_i + \sum_i^n (1/n) \Delta v_i$$

I
II

where χ_i is the mole fraction of and Δv_i the chemical shift difference in the n th form (rotamer). Applying it to a case at hand, Gutowsky demonstrated that the 'asymmetry effect' (the population-independent II term) could be sizeable. Raban (1966), besides

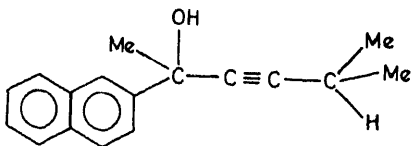
others, using a calculational procedure based on absolute reaction-rate theory developed by Newmark and Sederholm (1965), independently corroborated that the 'asymmetry effect' component could, by no means, be regarded as negligible.

Somewhat more recently, ROBM have examined the meaning of Gutowsky's partitioning of observed anisochrony into population-dependent and -independent terms and, more generally, of looking at geminal nonequivalence as originating either in conformer population difference or in 'intrinsic asymmetry'. The second factor arose not merely because terms like 'asymmetry effect', intrinsic asymmetry, 'inherent magnetic asymmetry', etc. had not been used to express a precise physical concept but also because Snyder (1966b) had specifically suggested that anisochrony of the sensors U , if found in a case like 10 would provide an unambiguous test

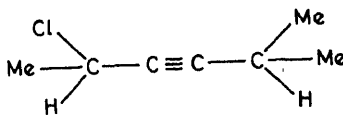


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for the origin of magnetic nonequivalence since any observed anisochrony of the U 's in such acetylenes 'must necessarily arise from magnetic asymmetry' because, in view of the large spatial separation of the two rotors, any barrier to rotation would be low and the rotation could be considered as 'free'. ROBM noted that the non-symmetry of $XYZC$, necessary for leading one to expect nonequivalence of the sensors, must entail the presence of at least one barrier, however low, i.e. the profile of the potential governing the rotation would not be absolutely flat. As cited by ROBM, this situation had clearly been envisaged earlier by Waugh and Cotton (1961) who wrote, 'It seems unlikely that in practice the asymmetry with respect to internal rotation required to produce magnetic nonequivalence would not also be reflected in some angular dependence of potential energy'. The presence even of a single, low, barrier can effect inequalities in the populations because, even if all molecules in the sample were in excited rotational states, much higher than the barrier (i.e. were in unbound rotational states), the probability of occupying each such state would be conditioned by its distance in energy from the corresponding ground state, a distance that would vary accordingly, as each dihedral is assumed or, in other words, there will be an angular dependence of the probability complementing the shape of the rotational potential profile. Both ROBM, and Jones and Stiles (1977), the former using ^1H spectroscopy and the latter employing ^{13}C NMR, succeeded in measuring the anisochrony of the geminal sensors in 11 and 12,



11



12

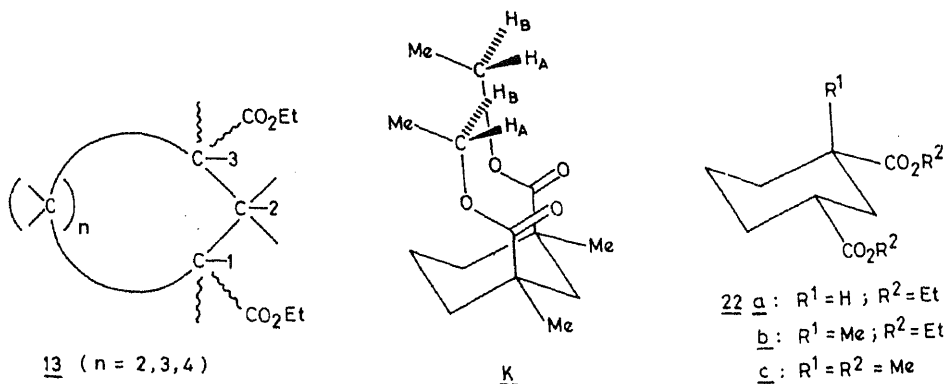
buted as exclusively arising from conformer population differences or from 'intrinsic asymmetry', the latter term and others like it (which have not been used consistently; for one usage see Jackson and Thapabinkarn 1975) be dropped, with the clear understanding that structures can be engineered, as originally suggested by Mislow and Raban (1967), where the need to partition observed anisochrony into population-dependent and -independent terms does not arise because, under conditions of fast rotation, systems with such structures can be considered as mixtures of three equally contributing populations of chiral entities with two sensors each. These are structures of the classes: $XYZCC(CU_2V)_3$, $R_3^*CCU_2V$ (where R^* is a chiral entity) and $R_3^*CC(CU_2V)_3$. Systems of the first two types have been synthesised and the anisochrony of the sensors in them detected and measured (Franzen and Binsch 1973; McKenna *et al* 1970; Morris *et al* 1973). The recommendation of ROBM attains validity because the division of observed anisochrony into population-dependent and -independent terms is entirely artificial: it is like merely stating that a number is the sum of two other numbers without being able to impose conditions limiting the values that the two component numbers may take. The matter would, of course, take an entirely different complexion if it were possible to calculate precisely what the screenings of the sensors U_A and U_B in 8a, 8b and 8c would be, how they would be modified when fast rotation is assumed and what the dependence on intermolecular interactions and solvent effects would be. There is not much hope of achieving this even though forays can be made into an understanding (Stiles 1977, 1979).

In the remaining part of this article we examine whether the observation of anisochrony of O-methylene protons of ethyl ester groups connected to chiral moieties may be employed to correlate certain structural features.

2. Three case-studies

2.1 A test diagnostic of configuration of cyclic 1,3-dicarboxylic ethyl esters

Some years ago it was suggested (Balasubrahmanyam and Sivarajan 1971, *bs*) that the magnitudes of anisochrony of H_A , H_B protons in diethyl esters of 5-, 6- and 7-cyclic 1,3-dicarboxylic acids (13) could be employed to assign configurations. The suggestion was prompted by the observation that the *cis* diester 14 exhibits, in the $-OCH_2-$ region



of its ^1H NMR spectrum, a pattern (figure 1) that is apparently the *AB* part of an ABX_3 system, symptomatic of the anisochrony of large magnitude of H_A and H_B while its *trans* analogue (15) shows an apparently normal 1 : 3 : 3 : 1 quartet (*AB*-nonequivalence undetectably small under the conditions of measurement); such difference in magnitude was regularly found in a number of instances (table 1) and its observation was used with reasonable confidence for assigning configurations (chemically confirmed in a few instances) to pairs of isomeric ethyl esters isolated in a study of the stereoselectivity of alkylation at C-3 of 6-cyclic 1-alkyl-1,3-dicarboxylic systems, carried out using various alkylating agents under various conditions (Radhakrishna 1976; Rao 1979; Jayaraj 1981; Narasimha Bharathi 1981).

The position prevailing at the time data presented in table 1 were being gathered was that observed anisochrony was constituted of a term due to 'conformer population differences' (CP) and a term due to 'intrinsic diastereotopism' (ID), the latter probably not having the same content as Gutowsky's 'asymmetry effect' (see above).

Arguing that, if ID were the major 'cause' of anisochrony, both the *cis* and *trans* diesters (14 and 15) should have exhibited anisochrony of like degree since the ester groups in them face the same type of chiral situation (α -carbons similarly substituted; cf. Elvidge and Foster 1964), as implied in their paper that a more acute CP imbalance was the 'origin' of the greater anisochrony in the *cis* case because that system may prefer the *syn* diaxial ester conformation K where considerable inter-ester nonbonded interactions may prevail and cause hindrance to rotations about bonds constituting the ester functions. Support for their conformational deductions was available, seemingly, from an inability to observe anisochrony of degree similar to that in 14 in the *cis* diesters 22a and 22b where the ester groups were very likely to prefer the equatorial dispositions shown and, therefore, free to populate various conformations in well-distributed manner. This argument was in line with the interpretation suggested by Mayer *et al* (1965, this work is referred to in greater detail later) for the observation that *O*-methylene anisochrony, found in a series of 10-ethoxycarbonyl-*trans*-decalins and Δ^8 -octalins, geminally substituted at C-1 (23a and 24a), disappears either on removal of geminal substitution at C-1 (23b and 24b) or on changing the hybridization at C-2 from sp^3 to sp^2 (23c and 24c). 'Constraints to rotation' (extreme biasing) about the C-10-ester axis and the OC-OCH₂ bond was thought to be necessary for observability of anisochrony since freedom to repopulate various conformations, less accessible when the spatial relationships were such as those depicted in L, would be restored to the CO₂Et group either when geminal substitution at C-2 is removed or when ring *A* assumes a flexible ('twist') form on C-1 becoming sp^2 hybridized (M).

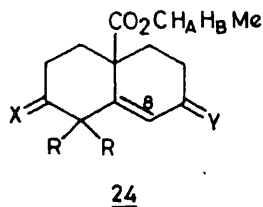
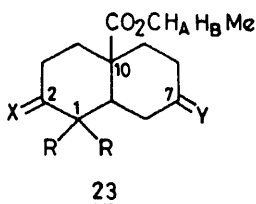
2.2 The behaviour of 'C-11' and 'C-12' triethyl esters

The need to bring the interpretations of the observations regarding the diesters 14 and 15 in line with current reasonings (ROBM) was clearly brought out by the behaviour of the triethylester 25c. This triester, prepared from a sample of the triacid 25a synthesized in these laboratories (Banerjee and Balasubrahmanyam 1968) and shown to be identical with a triacid ('C-11 acid') derived from abietic acid (26) by oxidative degradation (see Fieser and Fieser 1949), exhibited in its ^1H NMR spectrum (Sivarajan 1971) a normal quartet superimposed unsymmetrically on a typical nonequivalence pattern (figure 2); these resonances were assigned respectively to the C-2 ester -OCH₂- group and to the equivalently anisochronous *AB*-pairs of the flanking ester functions in

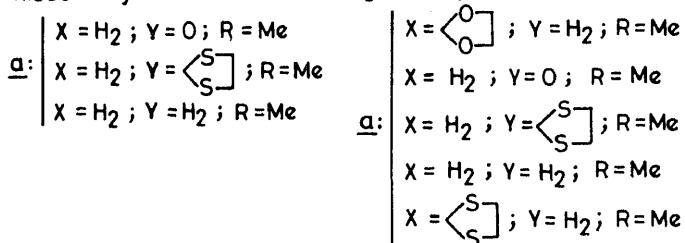
Table 1

System	Assigned configuration and $\Delta\delta$ (ppm)	Reference
 <u>14</u>	<u>cis</u> 0.15	Sivarajan (1971)
 <u>15</u>	<u>trans</u> 0.0064	
 <u>16</u>	<u>cis</u> 0.25 & 0.07*	Radhakrishna (1976)
 <u>17</u>	<u>trans</u> 0.07 & not observable*	
 <u>18</u>	<u>cis</u> 0.16	Jayaraj (1981)
 <u>19</u>	<u>trans</u> 0.05	
 <u>20</u>	<u>cis</u> 0.16	Rao (1979)
 <u>21</u>	<u>trans</u> 0.05	

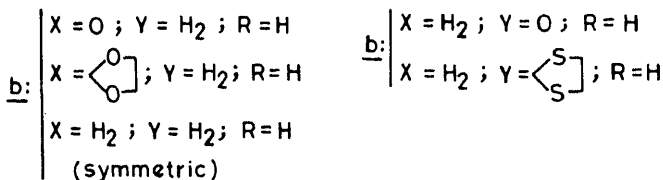
* Anisochronies not assigned specifically to either



Anisochrony of observable magnitude present in :



Anisochrony is of small magnitude (not observable) in



and in



accordance with the symmetry present in the structure (25a) of the precursor triacid (Barton and Schmeidler 1948, 1949). The magnitude of the anisochrony was similar to that in the *cis* diester 14.

The elucidation of the structures and stereochemistry of diterpene acids, typically represented by abietic and agathic acids, (26 and 27; see references under Ruzicka), can be said to have played a significant role in the formative period of ideas relating to biosynthesis not only of these substances but also of a host of other terpenic natural products (sterols, triterpenes) which were being simultaneously investigated (Fieser and Fieser 1949; Nicholas 1963). Much of the work related to the determination of the configurations of several substituted cyclohexane polycarboxylic acids derived in common from different series of alicyclic (terpenic) natural substances by oxidative procedures and serving to establish stereochemical relationships (Schaffner *et al* 1956). Among the observations leading to important generalizations was that the A/B ring junction in condensed alicyclics is nearly always *trans*, while the configuration at C-4 (steroid numbering), where one of the *gem* methyls may have been oxygenated (as in the diterpene acids), could be *R* or *S*. A/B *trans* fusion has received explanation in terms of

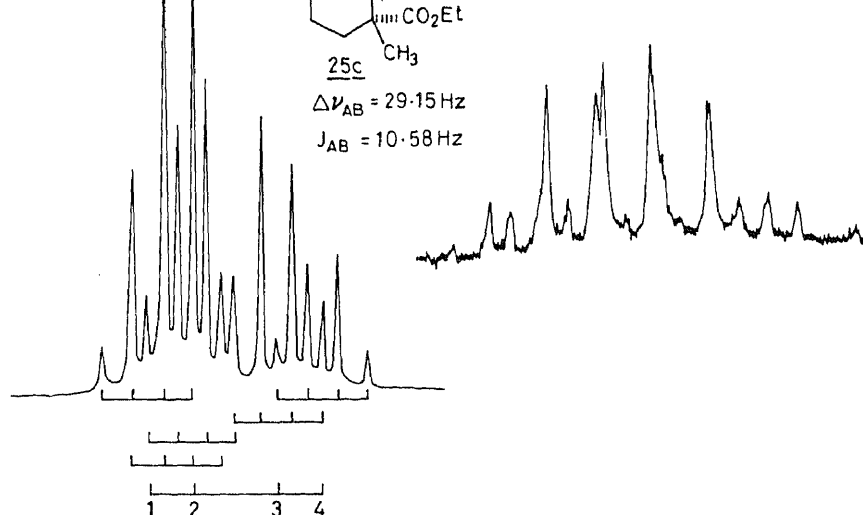


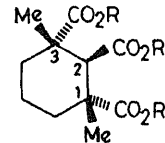
Figure 2. The O-CH₂ region of the 270 MHz ¹H NMR spectrum of triethyl ester 25c. **Inset:** The same region recorded with 100 MHz irradiation, reproduced for comparison with spectrum of diester 14 (figure 1).

oxide → triterpenes, protosterols) or protonation or halogenation (in marine organisms) of a double bond (Torsell 1983). The variation in the configuration at C-4 lies in the variation of the regio(stereo)selectivity of the oxidation of the C-4 geminal structure, which, therefore, must occur in a separate, enzyme catalyzed, step.

Among the substituted cyclohexane polycarboxylic acids that aided the establishment of configurational relationships in the diterpene acid field were the tricarboxylic acids 25a and 28a derived, respectively, from rings *A* of abietic and agathic acids. One may not be far off the mark in imagining that the elegant method that Barton adopted (Barton and Schmeidler 1948, 1949) for assigning relative configurations at C-1, C-2 and C-3 in the *meso,trans* form 25a led to the crystallisation of the basic concepts of conformational analysis (Eliel *et al* 1965). Barton's method comprised of comparing the difference parameters pertinent to successive ionization of the symmetric and unsymmetric monomethyl esters of the triacid 25a, and of the triacid itself, with those, as appropriate, of *cis* and *trans* cyclohexane-1,2- and -1,3-dicarboxylic acids (for details the reader is referred to Barton's original papers).

A very interesting salient to emerge from these studies was that, while the dianion derived from *trans* cyclohexane-1,2-dicarboxylic acid would prefer the diaxial conformation (29) in which a 'long' distance between the anionic centres prevails, the trianion derived from 25a would prefer the triequatorial conformation 30 in which 'short' distances prevail.

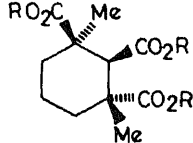
The trimethyl esters 25b and 28b of the isomeric triacids 25a and 28a had been synthesized in these laboratories via regiospecific and highly stereoselective methods starting from 2-ethoxycarbonylcyclohexanone (Banerjee *et al* 1966). The *meso,trans*



25 a : R = H

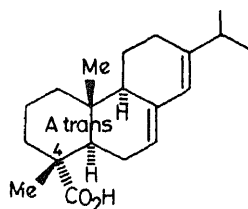
b : R = Me

c : R = Et

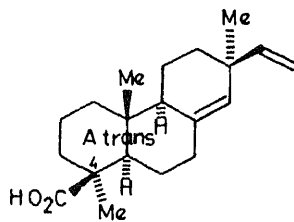


28 a : R = H

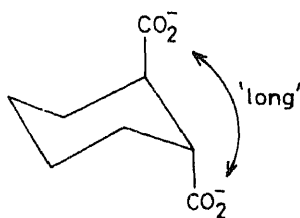
b : R = Me



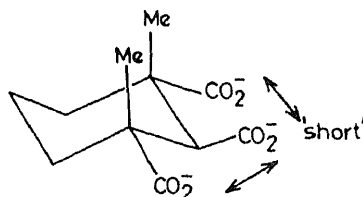
26



27

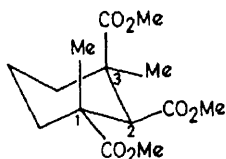


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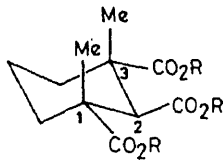


30

form 25b exhibited in its $^1\text{H NMR}$ spectrum (spectra reproduced in Banerjee and Balasubrahmanyam 1968) two singlets at δ 3.64 and 3.67 with an intensity ratio of 2:1 corresponding to 6H and 3H. Taking account of the symmetry of the structure 25b these signals were assigned respectively to the $-\text{OMe}$ groups of the ester functions at C-1 and C-3 and at C-2. As a result of lack of similar symmetry in the *cis,trans* case 28b, which may preferentially adopt conformation 31, three $-\text{OMe}$ singlets were found, at δ 3.64, 3.67 and 3.70. Occurrence of the first two at identical positions (at δ 3.64 and 3.67) in the two cases was seen as allowing assignment, respectively, to the C-1 equatorial tertiary and the C-2 equatorial secondary CO_2Me groups, the resonance at δ 3.70 then becoming available for assignment to the C-3 axial tertiary CO_2Me function, unique to the *cis,trans* case. However, assigning signals on such grounds does not have a sound theoretical basis and can probably be justified only because internal consistency is seen when once it is admitted that the equatorial ester conformation 32a is likely to be preferred by the triester 25b. But strong general support was available from the further observation (Sivarajan 1971) that the mono-C-methylated *cis* and *trans* dimethyl esters 22c and 33 exhibit $-\text{OMe}$ signals at δ 3.60 and 3.61 and at δ 3.60 and 3.64, respectively. If the conformational preferences are those shown, the factor of a secondary equatorial

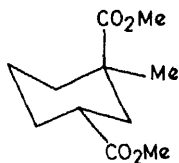


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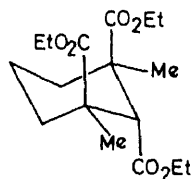


32a : R = Me

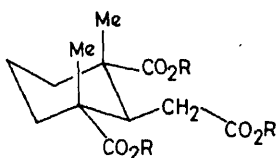
b : R = Et



33

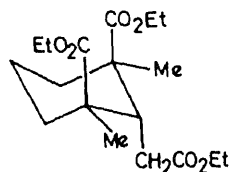


34



35a : R = H

b : R = Et



36

ester being common to both may be taken as indicating that the resonances at the identical chemical shift (δ 3.60) can be assigned to these groups, noting that, if the resonances that occur at δ 3.61 and 3.64 are, respectively, assigned to the equatorial tertiary ester in 22c and axial tertiary ester in 33, their relative shift would be consistent with what is found in the *meso,trans* and *cis,trans* cases 25b and 28b.

The assignment of the triequatorial ester conformation 32a to the trimethyl ester 25b, as discussed above, was consistent with the assignment of the conformation 30 to the trianion by Barton. However, if the conformational implications, discussed earlier, of the method (of bs) of assigning configurations on the basis of differences in magnitudes of anisochrony in isomeric pairs of cyclic 1,3-diester were valid, the triaxial ester conformation 34b should be assigned to the triethyl ester 25c because only in that conformation would the necessary interaction take place in order that the required cp imbalance be produced and anisochrony of order similar to that found in the *cis* diester K be induced. This assignment implied that, for both the method employed and the assignment of the triequatorial ester conformation 32a to the trimethyl ester to be simultaneously valid, one would have to presume that a change in conformational preference (from 34 to 32a) is concomitant to the conversion of a triethyl ester into a trimethyl ester, a proposition that seems very far-fetched (the difference between the ΔG°_{e-a} 's of CO_2Et and CO_2Me groups is miniscule (Hirsch 1967)).

It was pointed out (Nagaraja Rao 1974) that the problem arises because the method, as prescribed (bs), did not take into account the possible effect of a strategically located

anticipated as due to a change in configuration. In the case of the triethyl ester 25c such a group would be the centrally located ester function at C-2. Its role would be to generate a gradient of anisotropy as would induce anisochrony in the flanking ester functions comparable to that found in the diester 14 even when they are equatorially disposed and, because of this, whose internal, normally planar, conformation is unlikely to be skewed by extraneous factors. If the situation with the triethyl ester 25c is indeed that it prefers the triequatorial conformation 32b in the same manner as the corresponding trimethyl ester (32a) and that the observed high anisochrony derives from the presence of the anisotropic central ester function, it contrasts nicely with that encountered in one set of Mayer's bicyclic systems 23ab and 24ab where H_A , H_B anisochrony becomes of observable magnitude only because positioning a methyl *syn* axial to the C-10 ester function skews the population distributions within that function and about its bond with C-10 and not because an added anisotropic effect comes into play since replacing a C-H by C-CH₃ cannot materially affect the steepness of the gradient (ApSimon *et al* 1974; Usha 1984).

It is possible to provide independent and strong evidence that favours the equatorial preference in the triester 25b and incidentally demonstrate the correctness of the scheme suggested above for resolving the paradox in finding that presence or absence of a highly anisotropic ester function at C-2 makes for little difference in the magnitude of the anisochrony in the ester functions at C-1 and C-3 (*cf.* figures 1 and 2). The tricarboxylic acid 35a, homologous to 25a, is a co-product of the latter in the oxidative degradation of abietic acid (28) with alkaline permanganate (Ruzicka *et al* 1925), and it should have the configuration shown (Fieser and Fieser 1949). If the preferred conformation of its triethyl ester 35b is triequatorial, we have a situation where the source of perturbation is placed farther out than in the lower homologue 32b. Any consequent diminution in anisochrony, if found, would prove that preference in both 32b and 35b is equatorial because, had the higher homologue preferred the triaxial conformation 36 the anisochrony would not have significantly differed from that found in the diester 14 since extension of the side-chain at C-2 in the manner implied by that conformation would have scarcely been capable of influencing the mix of CP imbalance and anisotropy effects that contribute to the anisochrony in the diester.

The triethyl ester 35b showed in its ¹H NMR spectrum, as did its lower homologue 32b, a normal quartet superimposed unsymmetrically on a typical nonequivalence pattern (figure 3). The magnitude of the anisochrony was, however, much less.

Such fulfillment of expectation was, no doubt, gratifying but it forcefully brought out that even such examples as 32b and 35b are not an aid for asserting that the diminution of anisochrony was solely, or even largely, due to a lessening in the gradient of anisotropy since any residual CP imbalance which, in the case of the lower homologue 32b was more likely due to polar effects subsisting between the central and flanking ester functions rather than to steric interaction, would have been simultaneously diminished in 35b by the farther placement of the central ester function. It follows that, in comparing, for example, such pairs as the *cis* and *trans* diesters, 14 and 15, one should see the change in anisochrony accompanying the change in configuration as a composite and not assign it as originating in a change in a specific effect, CP or ID before and CP or anisotropy change after ROBM. The observation of an 'expected' magnitude of anisochrony could, however, retain value as an aid to configurational assignments (see

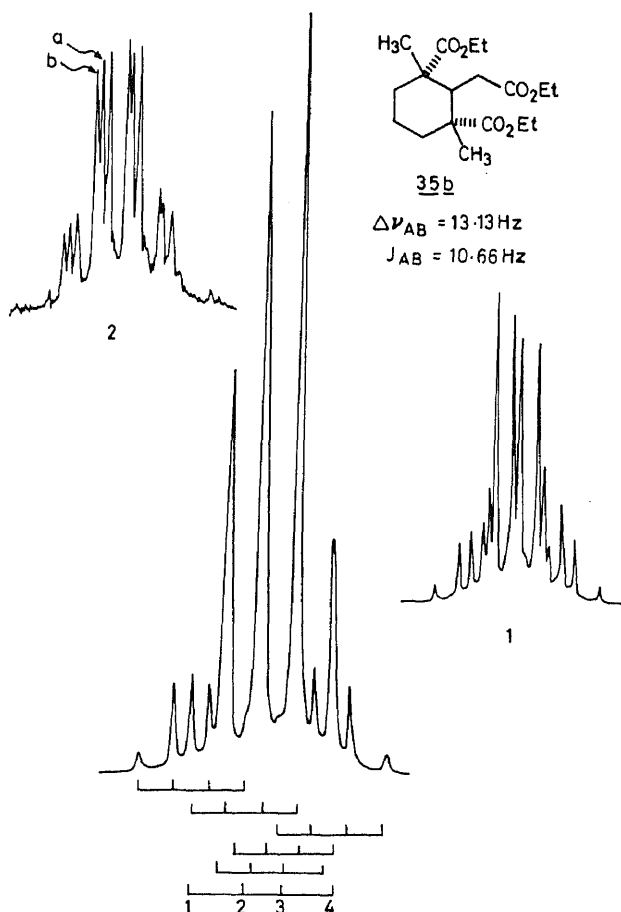


Figure 3. The O-CH₂ region of the 270 MHz ¹H-NMR spectrum of triethyl ester **35b**, homologous at C-2 with triethyl ester **25c**. **Inset 1:** The O-CH₂ region of the spectrum of mixed ester (C-1, C-3-Et and C-2-Me) corresponding to **35b**. **Inset 2:** The O-CH₂ region of the spectrum of **35b** recorded with the lower resolution obtainable under 100 MHz irradiation, reproduced in order to illustrate that the 'outer' quartets can be lost in noise while the 'inner' ones gain in intensity; note the progressive decrease in line-separation of the lines occurring upfield.

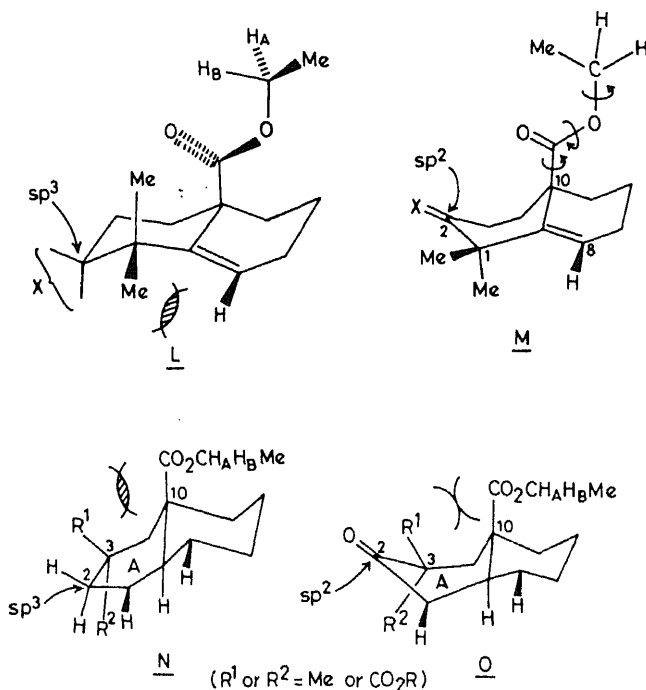
Sugimura *et al* 1971 for an example) provided the qualitative effects, at least, of the presence of population/anisotropy perturbing influences are borne in mind while comparing systems of related structure.

2.3 Structural factors in *trans* decalin- and Δ^8 -octalin-10-esters

The investigations of Meyer *et al* (1965) and those of the present authors (1966) of

in the gradient of anisotropy but from changes in the placements of H_A , H_B when rotations about the C-10-ester group bond and bonds within the ester group are biased in particular ways due to steric interactions. When first observed in cases like **23a** or **24a** the authors had assumed, in accordance with the then prevailing ideas and by analogy with findings in systems where more than two bonds separate the geminal entities from the chiral centre, that the anisochrony arises from the 'disymmetric environment in which the C-10 ethoxycarbonyl is placed' (i.e. the 'origin' of the anisochrony was in π). This interpretation became patently unmaintainable when it was found that anisochrony cannot be detected in the cases **23b** or **24b** where the C-1 axial (β) methyl has been replaced by a hydrogen (a change, we may note, that would be unlikely to induce any large change in anisotropy (ApSimon *et al* 1974). The presence of anisochrony in the C-1 β -methylated cases **23a** or **24a** was, therefore, reascribed to the steric influence of the axial methyl which, being larger than a similarly placed hydrogen, so constrains the C-10 ester function as to locate (accidentally!) H_A and H_B in highly different environments (**L**), thus favouring the detection of their anisochrony.

Subsequently it was found that the systems **23c** and **24c**, both with sp^2 hybridization at C-2, also do not exhibit detectable anisochrony, despite retaining the *gem* dimethyl substitution at C-1. The interpretation was that these 2-oxo derivatives go over to the flexible form of ring **A** (because flagpole-bowsprit interaction is diminished, Eliel *et al* 1965) where the 1 β -methyl cannot bias the conformation of the C-10 ester function in a manner conducive to the observation of large anisochrony since it (the methyl) is no longer in true axial orientation (see **L** $\rightarrow$ **M**, illustrated for the Δ^8 -case).



Effect less tangible when hybridization at C-2

The objection can now be raised that, since the carbonyl is a highly anisotropic group (Balasubrahmanyam *et al* 1983), its introduction may so modify the environment in 23c or 24c as to render H_A and H_B isochronous or nearly so and no conclusions regarding changes in ring *A* conformation would be warranted. It is pertinent, however, to recall that the change 23a to corresponding 24a, which introduces the probably highly anisotropic enone function, does not itself modify the observed anisochrony.

In the cases of the C-3 geminally substituted decalin systems* 18 and 19 we have found that anisochrony does not change when the C-2 methylene hydrogens are replaced by an oxo function (*cf.* 18 and 19 with 20 and 21, respectively; table 1). Considered in the light of the suggestions of Mayer *et al*, this result means that the spatial relationship between the 3β -group (ester or methyl) and the C-10 ester is not altered when the hybridization at C-2 changes from sp^3 to sp^2 . Barring an unlikely exactly compensating effect on the part of the newly introduced carbonyl, a legitimate deduction would be that twist (flexible) conformations of ring *A* are not significant contributors to the conformational equilibria in the cases of the oxo-compounds 20 and 21. This difference in behaviour, on relocating the geminal substitution from C-1 to C-3, could derive from the possibility that the equatorial methyl at C-1 interacts so strongly with the equatorial or vinylic hydrogen at C-8 in the C-1 geminal systems, 23a or 24a respectively, that ring *A* needs to assume a flexible form in their cases (e.g. L $\rightarrow$ M). If such need is absent in the C-3 geminal cases 18, 19 and 20, 21, the implication would be that relief of 1,3-*syn* diaxial interaction between the 3β -substituent and the C-10 ester function (N) is not an adequate cause for a similar transformation in ring *A* conformation ($\rightarrow$ Q) when the C-2 methylene is replaced by a carbonyl†. If these interpretations are taken as valid, the objection to Mayer's suggestions, stated above, cannot but be seen as ill-founded. At the same time it cannot be said that the diminution in anisochrony, seen when the *cis-trans* pairs 18 and 20 and 19 and 21 are compared (table 1), derives primarily or even largely from a directly caused change in the anisotropic gradient since exchanging a *syn*-axial ester function for a methyl at C-3 (changing the configuration from *cis* to *trans*) may also change the preferred attitude of the C-10 ester function and relocate H_A and H_B into an existent, less steep, gradient of anisotropy.

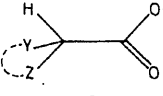
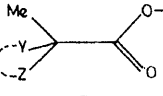
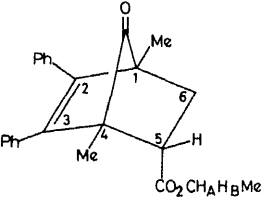
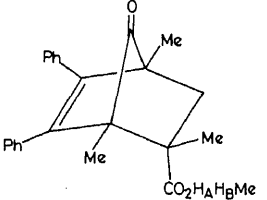
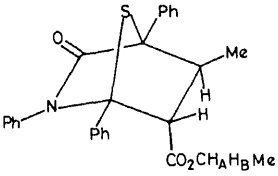
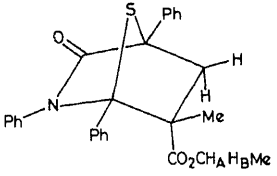
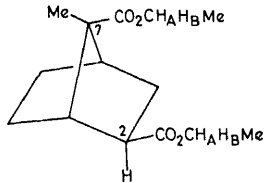
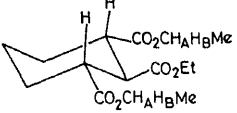
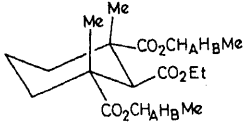
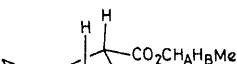
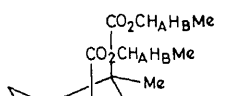
2.4 Effect of change in substitution at the chiral centre

In connection with ongoing stereochemical investigations there was occasion to prepare a number of chiral *sec*-(ethyl) esters S [with alkyl (1), alkyl (2) and H as the C- α substituents] and their α -methylated *tert*-analogues T [with alkyl (1), alkyl (2) and Me as the C- α substituents]. The uniform observation in these cases, as a glance at the relevant entries in table 2 would make apparent, was that the *sec*-esters exhibit lower anisochrony than their *tert*-analogues.

* In order to facilitate comparison, the numbering in systems 23 and 24 is retained for the cases 18–21; this continues to locate the bridgehead ethyl ester function at 'C-10'.

† The *peri*-interaction between the C-1 equatorial (α) methyl and the equatorial hydrogen at C-8 in 23a or the vinylic hydrogen at the same centre in 24a ($\equiv$ L) may be taken to be similar to the Me-H $A^{1,3}$ interaction which, according to one estimate (Johnson and Malhotra 1968), is *ca.* 6 kJ/mol. The transformation 23a $\rightarrow$ 23b or 24a $\rightarrow$ 24b (L $\rightarrow$ M) may relieve a large part of this interaction. The case with 18 or 19 is not likely to be similar. There is a possibility, already, of a departure of ring *A* from chair-conformation (N) that is not materially altered when transformation to Q (18 or 19, respectively, to 20 or 21) is considered since there is no large *peri*-interaction in need of relief.

Table 2

Systems $\Delta\delta_{AB}$ (ppm)		Reference
 <u>S</u>	 <u>T</u>	
 $\Delta\delta_{AB}$ 0.012 <u>45</u>	 $\Delta\delta_{AB}$ 0.188 <u>46</u>	Reddy (1975)
 Anisochrony reported not observed at 100MHz <u>47</u>	 $\Delta\delta_{AB}$ 'large'; actual value not reported; spectrum reproduced <u>48</u>	Potts <i>et al</i> (1974)
 Anisochrony not discernible for C-2 (sec) CO2Et at 60MHz; $\Delta\delta_{AB}$ 0.23 for C-7 (tert) CO2Et <u>49</u>		Reddy (1975)
 $\Delta\delta_{AB}$ 0.044 <u>50</u>	 $\Delta\delta_{AB}$ 0.14 <u>32b</u>	BB (1973); Narasimha Bharathi (1981)
		Narasimha Bharathi (1981)

This observation was at variance with the R  ch-Ugi group-theoretical treatment of the effects of asymmetry (R  ch and Ugi 1969, R  ch 1972) which Binsch employed to look into the possibility of correlating the magnitude of anisochrony with substitution at an asymmetric carbon (Binsch 1973; Capriol and Binsch 1979). In simple terms, the R  ch-Ugi approach implied that the effect of asymmetry should be related not to the properties of the ligands at the asymmetric centre but to the pair-wise differences in these properties. On this basis one would be led to expect greater anisochrony in a case where the substituents are less 'alike' e.g. *sec*-esters where the two alkyl groups (1) and (2) and H, than in a case where they are more 'alike' e.g. *tert*-esters where they are the two alkyl groups and Me.

It appeared that an explanation of our finding, contrary to expectation, had not been sought, reasonably, not by questioning the very validity of the R  ch-Ugi approach (Vigneron *et al* 1977, however) but by examining if Binsch's model, developed from systems which was representative enough to include the systems gathered in table 2. These systems differ in three respects from the structural type 1 from which the model was constructed, viz, the interposition of the carboxyl moiety between the chiral and prochiral centres, the absence of rotational symmetry in the ligands X, Y or Z about the connecting bonds and the presence of cyclic connectivity between a pair of ligands. One way to begin was to proceed in quest of a system where, despite the existence of these features, the observation would accord with expectation based on the model and to find the reasons thereof. We did find three such systems but before advancing our explanations we briefly review the development of Binsch's model and take note of certain early suggestions regarding anisochrony in chiral esters.

2.4a The Binsch heuristic: For constructing his model Binsch required representative values (including signs) of anisochronies in a set of structurally similar systems containing a chiral centre and prochiral sensor units. Binsch synthesized 10 chiral ethanes BrF_2CCXYZ (5) in which XYZ ran through all possible triads from the ligands H, F, Cl, Br and Ph. The anisochronies of the diastereotopic fluorines in the 10 rotamers, arising as three stabilizations ($8abc$; $U_a = U_b = F$ and $V = Br$) for each of the 10 compounds, were measured after lowering the temperature of the samples to levels requisite for 'freezing' the rotational equilibria. The free-energy differences between conformers, ΔG_{pq}° ($p = q = a, b, c$ with $p \neq q$; a, b, c as in structures 8a), were calculated for each of the systems from population distributions as found from the integrated intensities of the lines assigned to the individual conformers in the ^{19}F NMR spectra recorded at the low temperatures (Norris and Binsch 1973).

The transformation properties peculiar to chiral ethanes of type 8 allowed writing the sum rules,

$$\Delta G_{ab}^\circ + \Delta G_{bc}^\circ + \Delta G_{ca}^\circ = 0$$

and

$$(\lambda_x - \lambda_y) + (\lambda_y - \lambda_z) + (\lambda_z - \lambda_x) = 0,$$

in the second of which the scalar parameters λ represented measures of, as yet unassigned, properties of the ligands at the chiral centre on which the free-energy differences would depend. The proportionality relations

$$\Delta G_{ab}^\circ = f(\lambda_a, \lambda_b)$$

(where p, q are as before and $M = N = X, Y, Z$ with $M \neq N^*$), represented a heuristic point of view in that the λ 's could be made to have the meaning, 'characteristics of the ligands that contribute to the anisochronies in the different systems' by making the proportionality constant f have the dimensions of cube root of (energy/chemical shift) i.e.

$$f = (\Gamma_j/\chi_j)^{1/3},$$

where Γ and χ are the products, respectively, of the three ΔG° 's and the three differences $(\lambda_M - \lambda_N)$ in the case j of the m systems 8, all having the same U_A, U_B and V (viz, F, F and Br).

The heuristic model rested on the hope that a constant value of λ , characterizing each ligand M , would be found if the χ_j 's, the chirality functions, can be calculated. For this, the task was to find the global minimum of the functional

$$g = \sum_{j=1}^m (\langle \Delta_j \rangle - \chi_j)^2,$$

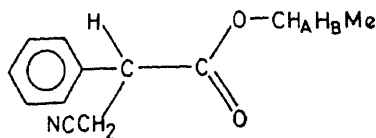
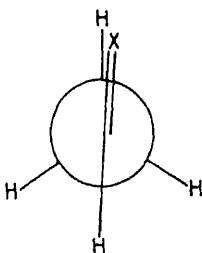
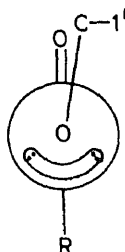
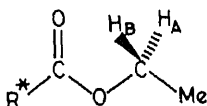
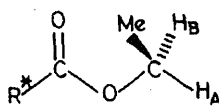
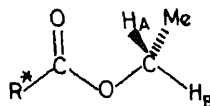
where $\langle \Delta \rangle (= \sum_r^{a,b,c} P_r \Delta_r)$ is the population (P_r) weighted sum of the anisochronies Δ_r of the contributing conformers r in the case j . The minimization, which also had the effect of reducing variations in the experimentally determined $\langle \Delta \rangle$'s caused by non-ideal $M\hat{C}N$ and M (or N) $\hat{C}C$ bond angles, changes in these angles as each conformation 8a, b or c was assumed, and measurement errors, was carried out using the so-called 'breathing grid' formalism and the hierarchy of the λ values was set by taking $\lambda_H (= 0)$ as the 'standard'.

Among several ways by which Binsch successfully tested this model the most incisive one was the demonstration that the λ parameters do govern the population distribution among the rotamers—agreement between this distribution, calculated on the basis of the parameters, and those obtained from line-intensities in the 'frozen' spectra showed an average deviation of just 4%.

Since χ , the chirality function, is the product of the *differences* between the λ parameters, taken pairwise, its value would increase with increase in value of the differences. Inasmuch as it begins to approximate numerically $\langle \Delta \rangle$, changes in observed anisochrony, when different systems (e.g. chiral ethanes) are compared, are to be perceived as reflections not of the properties (size, etc.) of the ligands at the chiral centre but rather of the pairwise differences in these properties—the more different the ligands the greater the effect, as already stated.

2.4b Snyder's suggestion: In order to explain the presence of $-\text{OCH}_2-$ anisochrony in β -ethoxycarbonyl- β -phenylpropionitrile 37, where no important external steric influences can operate directly on the ethoxy carbonyl moiety, Snyder (1966a) suggested an internal mechanism of transmission of asymmetric effects: In analogy with propene or acetaldehyde in both of which an eclipsed conformation (38) is stabilized (Karabatsos and Fenoglio 1970), an alkyl ester moiety may be stabilized in a conformation in which the O-alkyl bond eclipses the carbonyl (39). For ethyl esters the three staggered O-ethyl conformations 40a, b, c, for which $\text{O}=\text{C}-\text{O}-\text{CH}_2$ eclipsing has been assumed, can be considered. If R^* is not chiral the populations of 40b and 40c

* The correct maintenance of the $p, q-M, N$ correspondence as the cyclic permutations are taken also determines the signs of the ΔG° 's and λ 's.

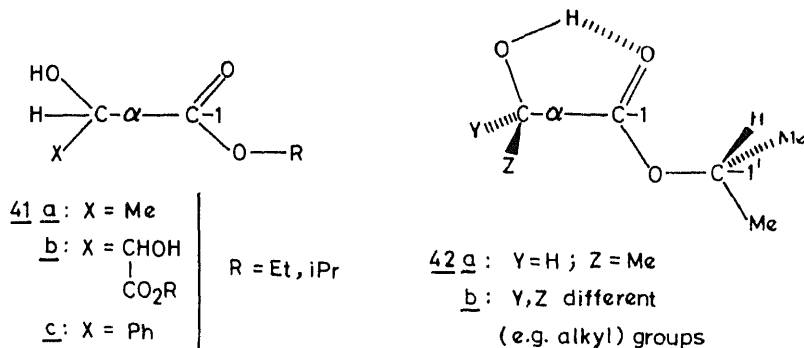
3738 (X = CH₂ or O)3940:abc

would be equal (and less than that of 40a because of Pitzer strain, *et al* 1965) and no anisochrony would be observable. On the other hand, if R^* is chiral an inequality would be induced in the populations of 40b and 40c (presumably by forces not dissimilar to those that act at an allylic centre and cause asymmetric induction when addition takes place at the double bond; references in Midland and Kwon 1983) and this inequality would lead to the observability of H_A , H_B nonequivalence.

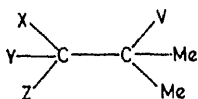
Analogy with propene or acetaldehyde (38) may not be strictly relevant but a considerable body of evidence now exists showing that *s-cis* forms (40) of alkyl esters are indeed considerably stabilized (Jones and Owen 1973; Vold and Vold 1974). And, one may take the view that Snyder's suggestion amounts merely to an extended way of stating the viewpoint that existence of diastereotopicity cannot be divorced from the conferment of inequality of populations (roBM; Waugh and Cotton 1961; Binsch 1973). Whether it contains anything that is of relevance only to esters 3 is examined later.

2.4c The interpretations of Bowman *et al*: Bowman *et al* (1965) synthesized a number of esters (e.g. 41) of α -hydroxy acids employing ethyl, isopropyl, etc. alcohols and prepared certain of their α -OH acylated derivatives required for a projected study. Salient results of this study were that (i) a higher degree of anisochrony is engendered when the α -hydroxy groups in lactates (41a) and tartrates (41b) are acylated by aromatic acids; (ii) the degree of dependence of anisochrony on temperature is higher in tartrates than in lactates; (iii) the anisochrony changes when the possibility of hydrogen-bonding between the α -hydroxy group and the ester carbonyl is removed.

These and similar results were interpreted largely in terms of departures from the single conformations (e.g. 42a for isopropyl lactate) in which the α -hydroxy esters were regarded as stabilized as a consequence of play of forces such as the preference for O=C—O—R eclipsing, hydrogen-bonding between the α -OH group and the ester C=O and the tendency on the part of the prochiral centre (C-1' in 42) to adopt a particular orientation with respect to the O—CO bond. Attempts were made to consider qualitatively possible changes in the differential shielding of the prochiral sensor units attendant on changing the substitution at the chiral centre C- α (e.g. acylation of the α -hydroxy group with an aromatic acid). But in the absence of possibility, then as now, of obtaining information of a quantitative nature on changes in shielding, efforts to extract conformational information from changes in anisochrony must remain in the realm of conjecture.

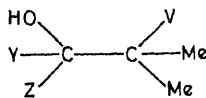


2.4d *A paper experiment*: This comment on the interpretations suggested by Bowman *et al* (1965) provides a context to address the interesting question whether the existence of an interaction between V and a substituent at the chiral centre, other than of a type that originates in a 'bulk effect', can be demonstrated solely by comparing anisochronies in ethanes of type 8. In the case of the halo-ethanes (5) considered by Binsch, orbital repulsion effects (repulsive interaction between filled orbitals), can be taken to have played the largest part in determining the values of the λ parameters, which, as a consequence would have reflected mainly the 'bulk effects' of the ligands. If, however, a specific (let's say attractive) interaction were to subsist between V and X in a given set of ethanes, the Binsch heuristic would lead one to expect a change in the ranges of variation of $\lambda_{X,Y,Z}$, had these ranges been established from a study of systems where V and the ligands X , Y and Z interact only in terms of orbital repulsion effects. Such apparent 'violation' would thus be predictable from the heuristic itself. Considering more specifically, one may envisage a 'paper experiment' where $\lambda_{X,Y,Z}$ are calculated for a number of isobutanes of type 43 which are classified into sets of constant V while X , Y , Z run through a large gamut of possibilities. It should now be possible to select those combinations of V , X , Y , Z , where the interactions are likely to be of a nature largely engendered by orbital repulsion effects, and establish ranges of variation of λ for each of the ligands X , Y and Z at the chiral centre. One then selects a set where an attractive interaction between V and one of ligands, say X , can be postulated and notes the placements of λ_X , λ_Y and λ_Z of this set with respect to their respective ranges of variation. The expectation would be that, while λ_X gets placed near the low end of its variation, λ_Y



43

(X,Y,Z varied; systems classified into sets under the V's)



44

(V's chosen to preclude hydrogen bonding with -OH)

and λ_z would become placed near *their* high ends. If the attractive $V-X$ interaction is strong enough, these λ 's (λ_y and λ_z) may even lie outside their 'normal' ranges. An example of an attractive $V-X$ interaction could be when $X = \text{OH}$ and V has a heteroatom favourably located for hydrogen-bonding. It is tempting to conclude that the question raised at the beginning of this paragraph can be answered in the affirmative. However, realization of this experiment would be difficult not merely because of the computational difficulties that might be encountered in establishing the global minimum of the functional g (see above) in all the cases but because of the really immense synthetic effort that would be needed.

One might now consider extending the experiment suggested above to the cases, for example, of isopropyl esters (42a) of α -hydroxy acids where hydrogen-bonding between the α -OH and ester-CO groups is a definite possibility (*cf* Vigneron *et al* 1977). The expectation here would be that the λ parameters would acquire such values as to show up the OH group as being 'smaller' than in cases such as isobutanes 44 where, with $X = \text{OH}$, V , Y and Z are so chosen that only orbital repulsion effects are at work. If this expectation is realized, it, to our minds, is the only way to demonstrate, although indirectly, what Bowman *et al* (1965) were apparently striving, in part, to demonstrate. It is important to note, however, that the assumption that populations about the $\text{O}-\text{C}-1'$ bond in 42 are not altered when Y and Z are changed, underlies the expectation. It may be argued that such an assumption is subject to the same disability as the suggestion due to Snyder (1966a) regarding the possibility of inquiring into the 'origin' of anisochrony by looking for its presence in chiral acetylenes of the type 10 ($n = 1$). As already discussed in the introductory section, the disability in that case pertained to the question whether rotation of the prochiral centre would be *absolutely* free or not. In the case of the assumption needed for the suggested experiment with the α -hydroxy esters (42) the question is not whether populations about the $\text{O}-\text{C}-1'$ bond remain absolutely unaltered when Y and Z are changed but whether they would be so drastically altered as to nullify the basis of the experiment. The answer to this last question would appear to be in the negative for the reason that in the zigzag and $\text{O}=\text{C}-1'-\text{O}-\text{C}-1'$ eclipsed conformation (42) of ester groups, field and steric interactions between the substituents at $\text{C}-\alpha$ and $\text{C}-1'$ are likely to be weak, and other conformations where they may acquire significance would only be very minor contributors to the conformational equilibrium. These arguments have a bearing on the discussions that follow.

3. The role of an α -methyl group—enhancement of anisochrony

Noting that the existence of small-to-medium connectivity between a pair of ligands at the chiral centre, that causes them to lose enantiomerism in a system, is a factor, it is

entries in table 2, one may consider whether some principle of general significance or applicability underlies the enhancement of anisochrony that accompanies the change $\underline{S} \rightarrow \underline{T}$.

(i) A difference in the anisotropic magnetic effects of C-H and C-Me is unlikely *per se* to induce the fairly large effects observed since, as earlier studies have indicated (ApSimon *et al* 1974), the anisotropic effects of the C-H and C-Me bonds are themselves small and any differences would probably be quite ineffectual.

(ii) If the origin of the most effective (local) anisotropy is close to the connected ligands Y-Z the change $\underline{S} \rightarrow \underline{T}$ may move the loci of the sensor units into a region having a steeper gradient of anisotropy. X-ray crystallographic evidence (Balasubrahmanyam *et al* 1981) has disclosed that the angle C-4-C-5-CO₂ in 46 (109.4°) is significantly smaller than the similar angle in 45 (113.1°), implying that the ester group, as a whole, is indeed brought nearer the phenyl rings, the most anisotropic groups in the structures, on methylation (broken line in structure E indicates the displacement).

(iii) A factor likely to be of major importance is the possibility of smoothing out of the potential profile for rotation about the C- α -CO₂ bond when the α -Me system $\underline{T}$ is compared with the α -H system $\underline{S}$. In the latter, conformations in which the H-C- α -C=O dihedral is low are likely to be preferred if the interaction between C=O and the other ligands (Y, Z) is largely of the orbital-repulsion type. It may just be coincidental that in all the α -H compounds assembled in table 2 such preference places the average positions of the sensor units in low gradients of anisotropy while the absence of or lesser preference for any particular C- α -CO₂ rotamerization in the α -Me compounds allows the two sensors to experience a greater mean difference in local field strengths.

Before considering how this may happen in the instances cited in table 2, the cases of methyl isobutyrate 51 and methyl pivalate 52, models, respectively, of α -H and α -Me esters, can be examined to see if the expected smoothing out of the rotational potential occurs at all. Available experimental evidence had been interpreted earlier (see works cited by de With 1973) as indicating that, while a preference for H-C-C=O eclipsing exists in the case of difluoroacetic acid 53, large amplitude librations around C- α -C=O are likely in trifluoroacetic acid 54. Using a semi-empirical approach (CNDO/2), de With showed that this interpretation would accord with the shapes of the energy profiles for rotation about C- α -C=O in the two cases. Since both C-F and C=O bonds are highly polar (Wolfe *et al* 1971) the situations with 53 or 54 could be quite different from what may be the cases with 51 or 52 where the rotors are the nonpolar isopropyl and *t*-butyl groups, respectively. Employing, however, the same semi-empirical approach as de With, we calculated enthalpies at 30° intervals of the dihedral for a 180° turn about C- α -C-1 in methyl isobutyrate and methyl pivalate, assuming a planar C-O-C=O eclipsing (*s-cis*) conformation for the ester function, idealized staggered conformations for the methyls and standard bond lengths and bond angles (see legend for figure 4). The emerging profiles, depicted in figure 4A, B, show not merely the expected smoothing in the case of pivalate but stabilization, also expected, of rotamerizations in which C=O eclipses C-H (as in isobutyrate) or C-Me (as in pivalate); besides, a deep minimum is found for the H-C-C=O antiperiplanar conformation in isobutyrate.

It is possible that there is a qualitative difference in the make-up of H_A, H_B anisochrony as is found in chiral ethanes (1) and in chiral ethyl esters (3). There have

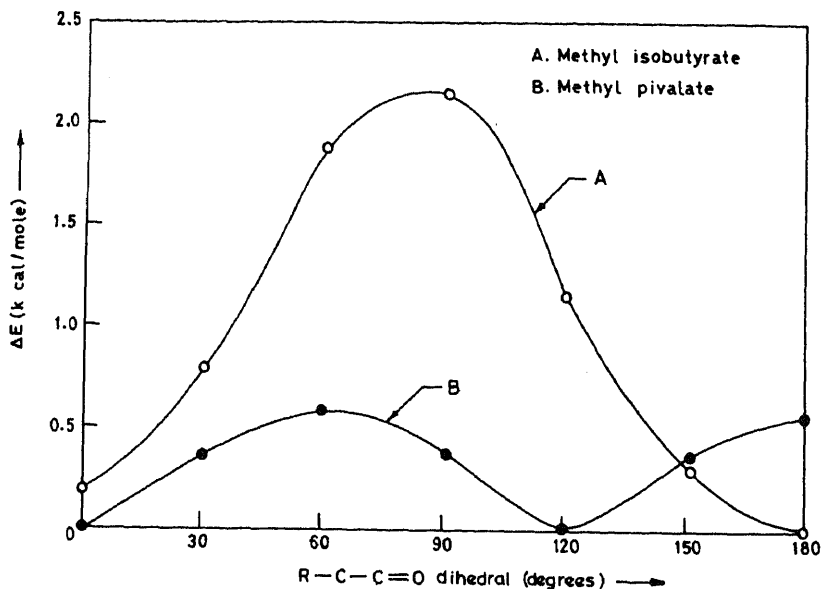
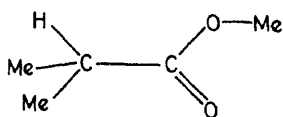
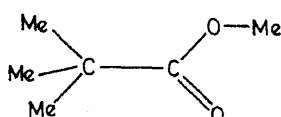
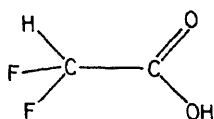
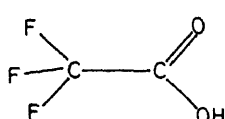


Figure 4. CNDO/2 rotational potential profiles of methyl isobutyrate 51 (curve A) and methyl pivalate 52 (curve B) for rotation about R-C- α -C=O. A planar conformation in which C=O eclipses O-Me and idealized staggered conformations have, respectively, been assumed for the ester functions and the methyl groups. Bond lengths (Å): C-H 1.09; C-C 1.52; carboxy C-O 1.36; ether C-O 1.46; and, C=O 1.22. Bond angles (°): C-C=O 116; O=C-O 124; C-O-C 113; and, all other angles consistent with tetrahedral distribution (109° 58') (O'Gorman *et al* 1950; Mathieson and Welsh 1965).

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been many attempts to correlate changes in observed chemical shifts (^1H , ^{13}C , etc.), attendant on changes in substitution at remote but effective centres, with changes in electron-density at the probe nuclei as calculated by MO methods (semi-empirical and *ab initio*). This subject has been extensively reviewed (e.g. Farnum 1975; Hehre *et al* 1976, 1977).

series of systems of closely related structure (e.g. *para*-C and H in substituted benzenes), the values of 'dependence factors' (ppm/e) have been found to vary over very wide ranges when different series are taken. While a part of the reason for this, and for the deterioration of correlation in many series, may lie in the approximations inherent to the MO methods (despite their increasing sophistication), the primary reason for what has been described as a 'general lack of correlation between electron-densities and chemical shifts' is that nuclear shielding is entirely too complex a phenomenon: ^1H shifts are subject to additional factors like magnetic anisotropic effects and electron-density changes at centres at which the probe protons are bonded and ^{13}C shifts to factors as can make for dependencies of opposite sign, and apparently of different degrees, on σ and π densities (Fliszar *et al* 1982). More pertinently to the subject at hand, one may expect that a difference in $1s$ densities between H_A and H_B in chiral ethanes 1 is not likely to remain constant during relative rotation of the chiral and prochiral rotors and that the rotamer-population weighted average of the difference would lead to the sizeable component of observed anisochrony, besides the component due to (the similarly averaged) differences in anisotropic effects to which H_A and H_B are subject.

We suggest that a qualitative difference can arise in the case of chiral ethyl esters 3 because the carboxy group can insulate the prochiral centre from the effects of the chiral centre. The intervention of the carboxy group is regarded as being capable of minimizing the electron-density difference effects while allowing anisotropy-difference effects free play so long as rotational preferences about the C-1-C- α bond in 3 persist (Stiles 1977; cf. ROBM). Recent work in our laboratories (Usha G and Premchandran R H, unpublished results) has shown that the insulation effect of the carboxy group is about as expected.

With chiral $\alpha\text{-H}$ and $\alpha\text{-Me}$ ethyl esters one may assume an *s-cis* conformation about C-1-O (3a) and antiperiplanar relationship between C-1-O and C-1'-Me (40a) and consider the possibilities schematized in figure 5: (i) the preference in the $\alpha\text{-H}$ case is as shown (A) or has H- α and C=O antiperiplanar, unless seriously perturbed by influences from Y, Z; (ii) α -methylation smoothes out the rotational potential about C-1-C- α (B) and rotamerizations about this axis become more equitably populated; (iii) 'external' influences from X, Y, Z, any or all of which may not be axisymmetric, ensure a particular preference (C) (Snyder 1966a). While the change A $\rightarrow$ B is likely to result, normally, in a reduction in the magnitude of H_A , H_B anisochrony, the change A $\rightarrow$ C (when X, e.g. Me, replaces $\alpha\text{-H}$) may increase or decrease it (relative to the $\alpha\text{-H}$ case) according as the major component of anisotropy normal to the C-1-C- α axis is in the direction p or is in the direction q , p possibly rendering it higher and q definitely rendering it lower.

The foregoing furnishes premises for considering the differences among $\alpha\text{-H}$ and $\alpha\text{-Me}$ systems in terms of attitude changes on the part of the ester function caused by the changes in the potential profile largely stemming from electron-delocalization-cum-orbital-repulsion effects. Other attitude-changing effects could be that $\alpha\text{-H}$ and $\alpha\text{-Me}$ systems are differently solvated by the same solvent or that a dipolar interaction between the ester carbonyl and one of the ligands is altered when $\alpha\text{-H}$ changes to $\alpha\text{-Me}$. The possible presence of such components and the difficulty of judging their importance relative to the type of changes implied by figure 5 do not prevent one from examining the specifics in the instances cited in tables 2 and 3 when looked at purely in terms of the types of difference that might arise between $\alpha\text{-H}$ and $\alpha\text{-Me}$ systems considered with the aid of that figure.

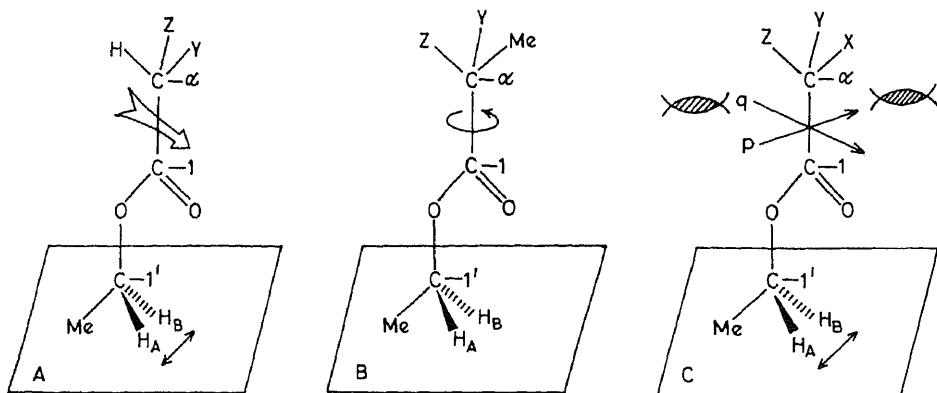
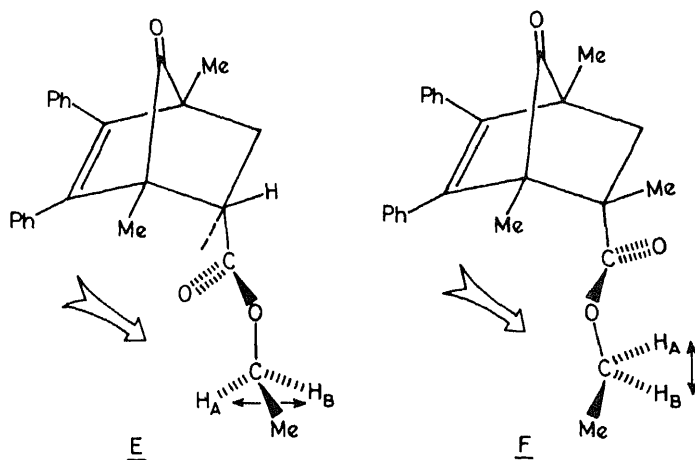


Figure 5. Residual anisotropic effects due to the presence of conformational preferences in ethyl $YZH(Me)C-\alpha$ acetates where Y and Z lack axisymmetry about Y or $Z-C-\alpha$ and hinder rotation about $C-\alpha-C-1$ by steric/polar effects (shaded areas in C). *Syn* $O=C-1-O-C-1'$ and *anti* $C-1-O-C-1'-Me$ preferences are assumed for the ester moiety. An additional assumption is that anisotropy, originating in Y, Z , has a large component in a given direction in the plane orthogonal to $C-\alpha-C-1$. **A** illustrates the possibility of H_A, H_B anisochrony being 'low' because H_A-H_B is perpendicular to the component gradient of anisotropy (arrow); **B** illustrates the possibility of anisochrony being diminished when anisotropy is better averaged by freer rotation about $C-\alpha-C-1$ as a consequence of α -methylation; **C** illustrates possibilities, other than **B**, that might arise when X changes from H to Me (or vice versa), changing the preference about $C-\alpha-C-1$ because constraints (shaded areas) change: when the component gradient gets set parallel (arrow p) to H_A-H_B , from being initially perpendicular (arrow q), anisochrony may become 'higher', even in an anti-Binsch manner (see text), when Me replaces H ; when the component gets set perpendicular, from being initially parallel, anisochrony becomes 'low' (cf Lyle and Thomas 1969).

Table 3

Systems $\Delta\delta_{AB}$ (ppm)	Reference
$\Delta\delta_{AB}$ (sec) 0.06 ; $\Delta\delta_{AB}$ (tert) not calculable ; 'outer' quartets not seen 57	Reddy (1975); Narasimha Bharathi (1981)
$\Delta\delta_{AB}$ 0.092 58	Narasimha Bharathi (1981)
$\Delta\delta_{AB}$ 0.052 59	
Doubled quartet at 100MHz	Rao (1979); Narasimha Bharathi (1981)
Anisochrony not observable	

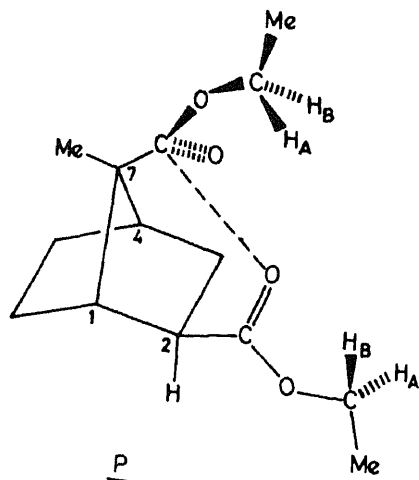
1. While it is entirely possible that the higher anisochrony found for the α (C-5)-methylated system 46 compared with its α -H analogue 45 is due to a relocation of the sensors into a steeper gradient of anisotropy, as already discussed, it cannot be but that a component of the difference arises from a simultaneous change in the attitude stabilized for the *endo*(C-5) ester moiety. Of two stabilized attitudes likely for the ester function in 45, the one in which the -OEt group is oriented away from the phenyls should be preferred (E). The alignment of H_A - H_B is likely to stay roughly at right angles to the drift of anisotropy originating in the general direction of the phenyl rings (the situation corresponds to figure 5Cq, even with $X=H$). Such preference would be conducive to the induction of anisochrony only in low degree. On methylation, the preference could alter to one in which the ester C=O eclipses either C-5-C-1 or C-5-C-6 (F; eclipsing of C-5-CH₃ by C=O could bring -OEt within possible short contact with the C-2 phenyl when the latter is in an orthogonal attitude during rotation). If there is no simultaneous drastic change in the preference about C-O-CH₂CH₃, H_A - H_B would become aligned roughly parallel to a large component of the anisotropic gradient and a higher mean anisochrony would be induced (the situation now corresponds to figure 5Cp with $X = Me$).



2. It would be reasonable to expect that the considerations set out above would be applicable, wholesale, to the pair of hetero-bridged systems 47 and 48, studied by Potts *et al* (1974) who observed '—an *exo* (α) methyl group is apparently necessary for the observation of nonequivalence—'.

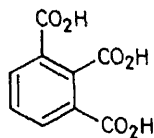
3. The norbornane *exo, syn*-diester 49 has the feature that both the *sec* and the *tert* ester groups form part of the same molecule. By means of preparing the mixed esters (C-2 CO₂Me and C-7 CO₂Et, and vice versa, Reddy 1975) it was possible to demonstrate that higher anisochrony is associated with the tertiary ethyl ester function at C-7. Since no question of redirection of the ester axis arises in this case one may directly look for differences in the rotamer preferences of the two ester groups, though the situation could be more complex than in 45 and 46 because polar interactions could play an important role.

A likely combination of conformational preferences for the ester functions, arrived at

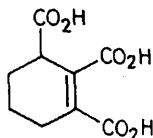


with the aid of molecular models, is depicted in P. The antiperiplanarity of the carbonyl of the C-2 (*exo*) ester with the C-2 (*endo*) hydrogen, in line with one of the stabilizations (180°) encountered in methyl isobutyrate (figure 4A), was thought to obviate steric crowding of the -OEt group, if the ester function were to adopt the opposite (0°) orientation. Similar reasoning leads to consideration of only two possible orientations for the C-7 (*syn*) ester function, ones in which the carbonyl eclipses either C-7-C-1 or C-7-C-4. Of these, the latter (shown in P) was considered preferred because the carbonyl would not then be oriented 'inward' towards the C-2 ester group. A favourable point in these relative orientations of the ester groups was that a possible attractive interaction could subsist between the negative carbonyl oxygen of the C-2 ester group and the positive carbonyl carbon of the C-7 ester group. If it is regarded that the chief components of the gradients of anisotropy affecting each ester function originate in the general direction of its opposite number, the situations with the C-7 and C-2 ester functions would, respectively, correspond with those given in figure 5C *p* and *q*; the alignments of H_A-7-H_B-7 and H_A-2-H_B-2 in the preferred conformations would be such that only the members of the first pair are subject to highly differing magnetic environments.

4. In an investigation of the contrasts anticipated in stereochemical results when hemimellitic and cyclohex-1-ene-1,2,3-tricarboxylic acids, 55 and 56, are catalytically hydrogenated it was necessary to estimate the isomer composition of the cyclohexane-1,2,3-tricarboxylic acids formed. The mixtures, as obtained from the hydrogenation, were esterified with diazomethane and the products were analyzed by gas chromatography. The assignment of configurations to the detected isomeric esters was based on



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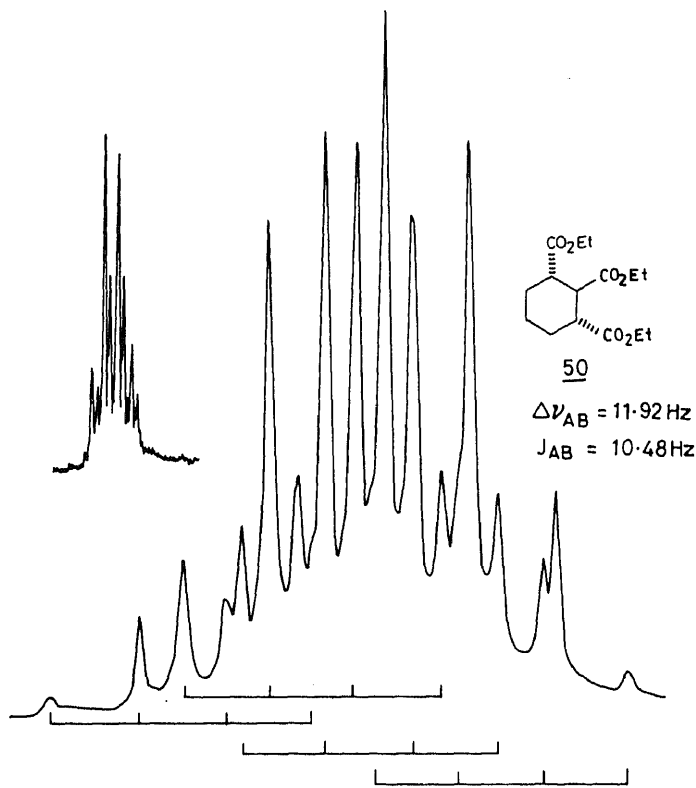


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the equivalence, by symmetry, of the C-1 and C-3 -OMe groups in the *cis,meso* and *trans,meso* forms and the nonequivalence of the three -OMe groups in the *cis,trans* form; more complex criteria were used to distinguish the first two (Balasubrahmanyam and Balasubramanian 1973; BB).

The triethyl ester of the product to which the *trans,meso* configuration had been attributed showed, in the -OCH₂-region of its ¹H NMR spectrum recorded at 60 MHz, what was apparently a pattern consisting of two overlapping sets of 1:3:3:1 quartets in the intensity ratio of 2:1 in the order of increasing field strength (see inset of figure 6). By symmetry, these seemed assignable, respectively, to the C-1, C-3 equivalent pair of -OCH₂-groups and to the C-2 -OCH₂- group. On the basis of comparison with the situation in the *cis* diethyl ester 14, already discussed, the equatorial ester conformation 50 seemed indicated, taking that geminal anisochrony, expected of the C-1, C-3 O-methylenes, was so low as to have been virtually undetectable.

An alternative interpretation of the -OCH₂- signal pattern could have been that it



consisted of a system of four 1:3:3:1 quartets (*AB* part of ABX_3), arising from geminal anisochrony in the C-1 and C-3 pair of $-OCH_2-$ groups, of which only the 'inner', more intense, pair was visible (*cf.* figure 3 relevant to system 35b) and that the quartet due to the C-2 O-methylene was accidentally isochronous with the low-field member of the pair. However, this interpretation seemed less tenable because, with the separation found for the 'inner' quartets (≈ 4 Hz at 100 MHz), the 'outer' ones would have had about 20–30% of the intensity of the 'inner' ones (analysis of *AB*-spectrum; Bible 1965) and unlikely to have been lost in noise. Despite this it was thought necessary to place the first interpretation on an independent and firm basis by demonstrating the presence of anisochrony by rerecording the spectrum of 50 under conditions of better resolution. As can be judged from the $-OCH_2-$ region of the 270 MHz spectrum reproduced in figure 6, the low-field (intensity 2) 'quartet' of the 100 MHz spectrum has been resolved into an *AB* quartet of 1:3:3:1 quartets, confirming the correctness of the interpretation suggested by 88 by which this 'quartet' was assigned to the C-1 and C-3 pair of $-OCH_2-$ groups and the high-field (intensity 1) quartet to the C-2 $-OCH_2-$ group.

It is of interest to recall here that diethyl ester 22a exhibits no discernible anisochrony even with 270 MHz irradiation i.e. anisochrony is less than 0.5 Hz at 270 MHz (Narasimha Bharathi 1981). This observation points not merely to the necessity of assigning the *syn* diaxial ester conformation **K** to diester 14 but to the importance of the role the central (C-2) ester function plays in 50 in providing the gradient of anisotropy required to induce anisochrony observed in that triester where, as is most likely, the conformational preference of the ester functions is equatorial (*cf.* earlier discussion of the cases 32b and 35b).

The triesters 50 and 32b then constitute another pair where α -methylation confers increase in anisochrony. While it is possible that the C-1 and C-3 ester functions in 50 have high preference for conformations in which α -H eclipses either C=O or $O-CH_2$, rotation of the similar functions in 32b may have low barriers at the destabilizations, in analogy with the transformation isobutyrate $\rightarrow$ pivalate. It cannot, however, be deduced, in the manner essayed with the earlier instances from table 2, that the sensor protons in 32b experience, on the average, more highly differentiated field-strengths than in 50 since rotational preferences of the ester functions, vicinally placed as they are in these triesters, are beyond qualitative assessment in view of the possibility of complex dipolar interactions and it would not be clear whether preference would correspond to *C_p* or *C_q* schematized in figure 5 in the case of any of these functions.

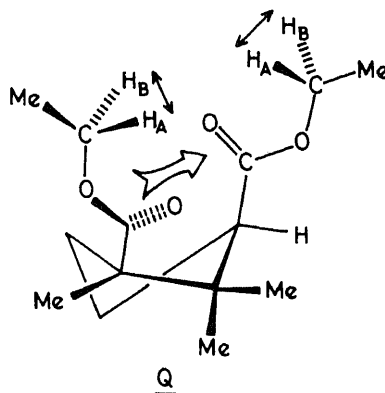
4. The role of an α -methyl group—attenuation of anisochrony

The lines of argument employed above have had, as a general *starting* premise, that a *sec*-(ethyl) ester function is likely to prefer either of two orientations, ones in which either C=O or $O-CH_2$ eclipses α -H, while a *tert*-ester function prefers no particular orientation since, in its case, stabilizations (which occur whenever C=O eclipses a C- α -C- β bond) are separated only by low barriers (figure 4B). In the instances treated so far an 'external' steric influence has been seen as hindering the normally comparatively freer rotation of *tert* ester groups, the particular rotational preference imposed by such influence inducing, accidentally, anisochrony higher than in the *sec* analogue.

explaining the cases of *sec-tert* ester pairs where the opposite phenomenon, viz. higher anisochrony in the *sec* cases, is observed. Two situations can be envisaged: it could be that the preference externally imposed on the *tert* ester group is such that the sensor protons become placed, on the average, in similar environments or that, in the absence of an externally imposed preference, the *tert* ester group is freer to rotate and the field strengths at the sensor protons get averaged in a manner that diminishes anisochrony.

In table 3 are listed three *sec-tert* systems in which anisochrony is higher in the secondary case than in the tertiary. Since the observation was in accordance with the Binsch heuristic, read in the terms 'anisochrony in ethanes 8 would be higher when *XYZ* are less "alike" than when they are more "alike"', these system pairs were considered as of no special interest at the time they were first examined. The statements made in the last paragraph, and the examples cited, have, however, made it clear that each comparison must be made on its own special merits. The systems mentioned in table 3 are, therefore, re-examined.

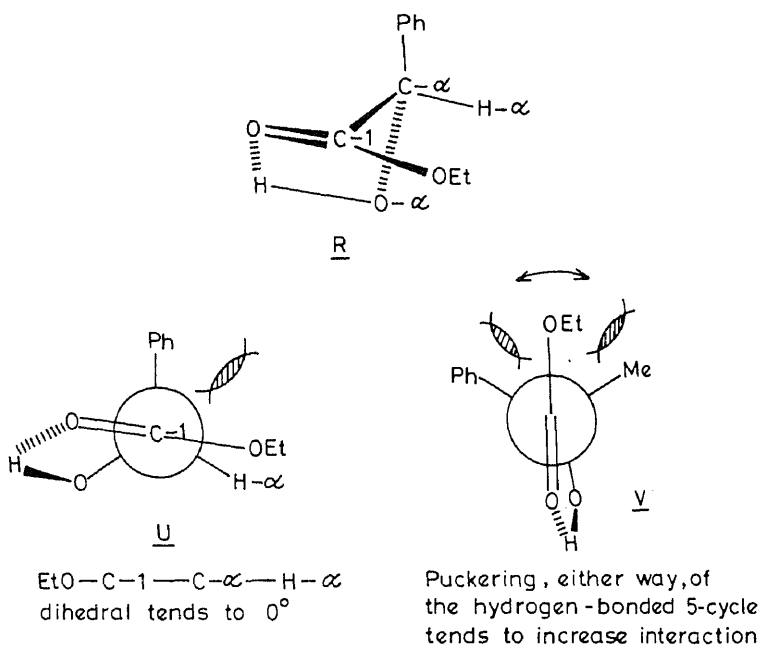
1. Diethyl camphorate 57 resembles the bicyclo[2.2.1]heptane diester 49 in having both the *sec*- and *tert*-ester functions in the same molecule in *syn* configuration but differs from it in that pseudorotation is possible to a conformation in which rotation of the ester function would, apparently, be freer. As with 49, the $-OCH_2-$ anisochrony pattern sets were assigned by comparisons with the 1H NMR spectra of the mixed esters. The pseudorotation judged with the aid of molecular models as offering the least hindrance to ester rotation and seeming to offset eclipsing interactions amongst the substituents on the cyclopentane ring to the maximum extent is represented in Q. It could be presumed, again, that anisotropy local to one ester function would have its chief origin in the other, with, perhaps, a slight shift towards the *syn* vicinal methyl group. The preferred rotamerization of the *sec*-ester function is likely to be one in which $O-CH_2$ eclipses $\alpha-H$ on the account that the $O-Et$ group would not be turned 'inward', as would happen were $C=O$ to eclipse $\alpha-H$. With such preference the probable placement of the O -methylene proton would be at points of differing magnetic field strength along a gradient of anisotropy. With freer rotation possible for the *tert*-ester group, a better averaging of the magnetic field strengths should diminish anisochrony in its case.



2. Ethyl mandelate (58) and ethyl atrolactate (59) are a pair of esters where attraction-dominant (e.g. hydrogen-bonding between carbonyl and hydroxy oxygens)

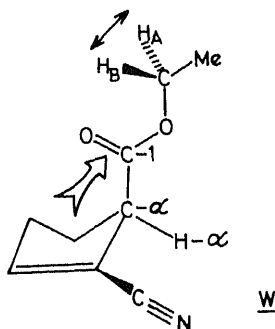
and repulsion-dominant (e.g. eclipsing of Ph by $-\text{OEt}$) interactions may condition the rotational preference of the ester function about the $\text{R}-\text{CO}$ bond. What follows is an illustration of the possibilities that might account for the higher anisochrony in the *sec*-case (mandelate).

The 5-membered cycle R constituted by H-bonding is not likely to be planar in mandelate (58) for the reasons that $\text{O}-\alpha-\text{H}$ would prefer to maintain antiperiplanarity with $\text{C}-\alpha-\text{H}$ and $\text{C}-\alpha-\text{Ph}$ *gauche* relationship with an $\text{O}-\alpha$ 'lone-pair' since a $\text{C}-\text{Ph}$ bond can be taken to be more polar than a $\text{C}-\text{H}$ bond (*cf.* the 'Edward-Lemieux Effect' Wolfe *et al* 1971). The effect of puckering of the type shown in R is to close the $\text{H}-\alpha-\text{C}-\alpha-\text{C}-1-\text{OEt}$ dihedral and to bring the carbonyl oxygen into antiperiplanar relationship with $\text{H}-\alpha$ (conformation R and projection U). If the potential in mandelate for an $\text{H}-\alpha-\text{C}-\alpha-\text{C}-1=\text{O}$ dihedral of $\approx 180^\circ$ is similar in shape to that of isobutyrate near 180° (figure 4A), conformation U may be regarded as specially favoured.



The case of atrolactate is qualitatively different, such singular preference being unlikely. Puckering either way (V) of the H-bonded 5-cycle would increase the enthalpy of the system because the $\text{EtO}-\text{C}-1-\text{C}-\alpha-\text{Ph}$ (or Me) dihedral decreases (*cf.* pivalate; figure 4B). Though H-bonding energy could be compensatory, the overall effect would be to flatten out the potential profile which, if the analogy with pivalate is valid, is not likely to be characterized by high barriers (*cf.* the contrast between pivalate and isobutyrate, figure 4B, A). Insofar as the likelihoods are that the ester group in mandelate has a particular rotational preference (U) and that in atrolactate has none (V) an explanation emerges why anisochrony is higher in the former, assuming, of course, that the anisotropic situation in mandelate leads to a higher anisochrony than does the

3. Such arguments seem transferable to the pair of unsaturated cyano esters 61 and 62. If the ene-nitrile moiety in these systems acts as the chief originator of anisotropy but offers little by way of polar effects capable of perturbing the conformational preference of the ester function (in any case the polar effects may be expected to operate in similar fashion in the two cases), two particular rotamerizations, those having $\text{O}=\text{C}-\text{C}-\text{H}$ dihedrals close to 0° and 180° , can be taken as preferred in the α -H system 61 and no particular one in the α -Me system 62. One can then account for the higher anisochrony in the former. It is to be noted that the $\text{H}_\text{A}-\text{H}_\text{B}$ line in the α -H system remains parallel to the probable direction of the chief component of the gradient of anisotropy at either the 0° or the 180° $\text{O}=\text{C}-\text{C}-\text{H}$ dihedral (W).



$\text{H}-\alpha-\text{C}-\alpha-\text{C}-1=\text{O}$ dihedral $\sim 180^\circ$ in 61 ; main gradient of anisotropy (arrow) parallel to $\text{H}_\text{A}-\text{H}_\text{B}$.

5. Temperature-dependence of anisochrony

The temperature-dependence of anisochrony can be regarded conveniently with the aid of the chiral ethanes 1. At a low enough temperature one may detect and resolve lines due to the prochiral sensor units U_A and U_B in the individual conformers (e.g. 8) that have lifetimes of necessary duration. At a temperature characteristic of each system 1 these lines will coalesce into two lines (or two sets) whose separation is the time-averaged anisochrony $\langle \Delta\delta \rangle$. At coalescence, and beyond, the residence time at each conformation will be short on the NMR time-scale and it becomes permissible to replace time-averaging by Boltzmann averaging i.e. Boltzmann distribution weighted by the population at each conformation which, in the case of chiral ethanes, can be specified by the dihedral between the rotors XYZC and $\text{CU}_\text{A}\text{U}_\text{B}\text{V}$, taking θ at $\text{X}-\text{C}-\text{C}-\text{V}$ eclipsing, for example, to be zero. Boltzmann averaging is expressed by the relation:

$$\langle \Delta\delta \rangle = \frac{\int_0^{2\pi} \Delta\delta(\theta) \exp[-V(\theta)/RT] d\theta}{\int_0^{2\pi} \exp[-V(\theta)/RT] d\theta},$$

where $\Delta\delta(\theta) [= \delta_{U_\text{A}}(\theta) - \delta_{U_\text{B}}(\theta)]$ is the U_A , U_B -anisochrony in the conformer with dihedral θ , $V(\theta)$ is the potential energy of that conformer and T is, for now, the coalescence temperature (expressed in K) characteristic of the system.

The variation of the potential energy with the dihedral [$V(\theta)$] is continuous and periodic and can, in general, be resynthesized from Fourier components, among which non-idealities in the geometries of the conformers (Stiles 1977) can, in principle, be included. Population weighted Boltzmann averaging implies that, with rise in temperature beyond coalescence, the sign and magnitude of $\langle \Delta\delta \rangle$ will be conditioned by the signs and magnitudes of the $\Delta\delta$'s of the initially less favoured conformations whose population-densities increase. No general statement regarding the behaviour of time-averaged anisochrony with changes in temperature in the region higher than coalescence would, therefore, seem warranted (for an example which exhibits complex behaviour see Jennings *et al* 1977).

It is instructive to consider systems where the substituents at the chiral centre themselves show dynamic behaviour in the sense that densities of different conformations internal to each substituent continue to change with temperature-change in the post-coalescence region. In the series of ethyl esters 14 (= K), 25c (= 32b) and 35b the inverse dependence of anisochrony on temperature, taken for all practical purposes as being linear within the ranges studied, increases down the series (figure 7). It is believed that this observation does not have a basis in mere accident and the attempt here is to examine its possible explanation in relation to the concept of 'increasing conformational mobility'.

In system 63, studied by Pavlik *et al* (1969), two sets of anisochrony patterns are seen

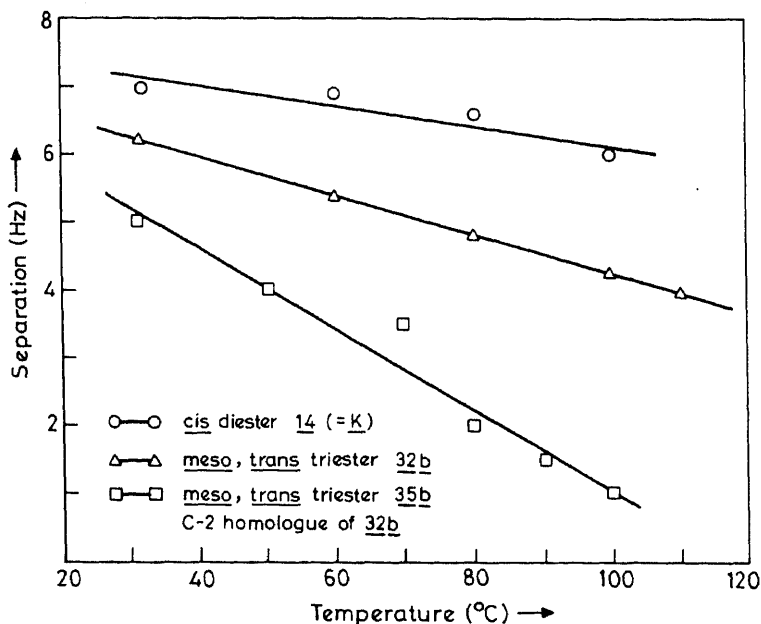
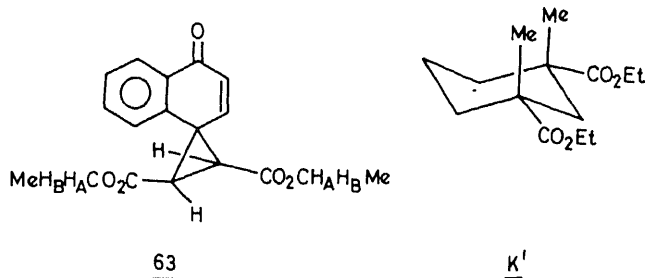


Figure 7. Variations in anisochrony with temperature-change in diester 14 and triesters 32b and 35b. 'Separation', used as the ordinate, represents the chemical shift difference in Hz at 100 MHz between two corresponding sharp lines belonging, one each, to the two 'inner' quartets (e.g. lines marked 'a' and 'b' in Inset 2 of figure 3) of the anisochrony pattern. This was used as a measure of $\langle \Delta\delta \rangle$ for convenience. The full lines represent least square fits. Spectra recorded were of solutions of samples in CCl_4 taken in tubes cooled under reduced pressure.

observed in this case one may suggest that, in their relatively unhindered environments, the ester groups populate various conformations to extents conditioned only by a potential field unlikely to be characterized by minima which differ widely in energy. Hence differences among the populations occupying these minima, hardly change with temperature (the alternative 'explanation' could, of course, be that $\Delta\delta$'s are the same or nearly the same in all the attainable conformations and there can be no variation of $\langle \Delta\delta \rangle$ with temperature, whether there are conformer-population density changes or not).



In the case of diester 14 indications are that the energy-minimum associated with the normal representation (conformation) K would much lower than that associated with its ring transform K' (see earlier pertinent discussions). Despite the possibility that $\langle \Delta\delta \rangle$ could be much smaller in the latter (see discussion vis-a-vis systems 22a, b), the temperature-dependence in 14 is not large in comparison with those in systems 32b and 35b. The argument that K' never gets largely populated is persuasive.

In the triesters 32b and 35b the central (C-2) substituent is thought to have the moderating influence of lowering the energy differences between the ring transforms 32b and 34, and 35b and 36, taken as the largest contributors to the conformational equilibria; it is possible that the activation barriers are also lowered. Contributions from forms, besides the said ones which are extremal, in which rotations of the ester functions are less hindered and in which the gradients of anisotropy are simultaneously lower, can increase the temperature-dependence of anisochrony in these cases. Between the triesters 32b and 35b greater conformational mobility can be assumed in the latter where the central ester function, the modifier of the local gradient of anisotropy as well as the originator of important polar/steric influences, is placed farther out by the intervention of the methylene. A greater degree of averaging becomes possible and the temperature-dependence of anisochrony becomes yet higher.

6. Concluding remarks

Differential screening of prochiral sensor units packs a wealth of information. Quantitative unravelling of the contributions of the individualized effects is not yet within reach of shielding theory. Comparisons of magnitudes of time-averaged

anisochrony of O-methylene protons in ethyl ester units connected to differently structured chiral entities is thought to have permitted, however, the qualitative assessment that changes in magnitude derive primarily and largely from reorientations of the H_A-H_B line with respect to the 'largest gradient of anisotropy' while other factors, though remaining effectual, assume lesser importance as modifiers of the magnitude.

Acknowledgement

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Oxidation of substituted phenols with metal dioxygen carrier, Co(salen)pyridinate: solvent effects†

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Abstract. The course of the oxidation of substituted phenols with Co[bis(salicylaldehyde)ethylenediimine]pyridinate-dioxygen complex is found to be dependent on the nature of the solvents used. The various oxidation products of 2,6-dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone in chloroform and methanol solvents have been isolated and characterized. Plausible intermediates leading to these reaction products are discussed.

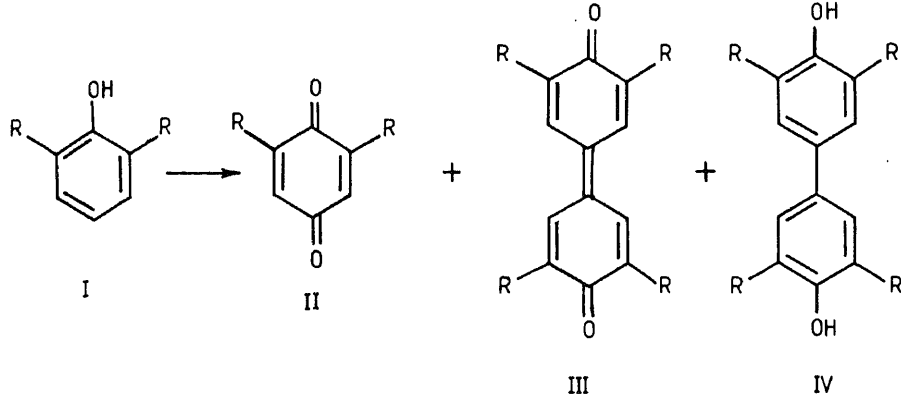
Keywords. Oxidation; metal-dioxygen adduct; substituted phenols; cobalt bis(salicylaldehyde) ethylenediimine pyridinate.

Introduction

In the course of an earlier study on the oxidation of 2,6-di-*t*-butylphenol with various metal chelate-dioxygen complexes, it was observed that Co(salen)Py [salen—bis(salicylaldehyde)ethylenediimine] is an efficient oxygen carrier and that variation in the structure of the metal chelate had a pronounced effect on the nature of products formed (Satish *et al* 1985). The present study concerns the effect of solvents viz. chloroform and methanol on the oxidation of 2,6-dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone using Co(salen)Py-O₂ complex under homogeneous conditions.

Results and discussion

Oxidation of 2,6-dimethylphenol (**Ia**) with molecular oxygen in the presence of Co(salen)Py as catalyst in chloroform and (methanol) as solvent (25°C, oxygen pressure 10 g/cm², 6 hr, catalyst to substrate ratio 1:20) gave 2,6-dimethyl-1,4-benzoquinone (**IIa**) 57.4% (59.1%); 3,3', 5,5'-tetramethyl-4,4'-diphenoquinone (**IIIa**) 1% (4.1%) and 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (**IVa**) 4% (3.6%) (scheme 1). The formation of products can be explained on the basis of well known metal-dioxygen adduct mechanism (Zombeck *et al* 1981). Benzoquinone **IIa** is formed by transfer of an oxygen atom from the metal-dioxygen adduct to the phenoxide radical, whereas **IIIa** and **IVa** arise from the coupling of two phenoxide radicals. Product distribution was essentially similar in both chloroform and methanol. However, oxidation of 2,6-di-*t*-butylphenol



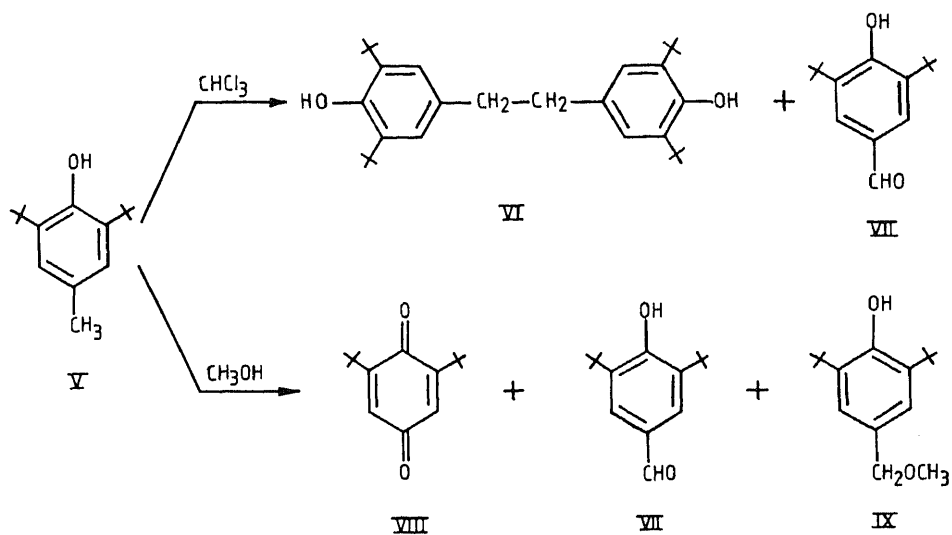
- a, R = $-\text{CH}_3$
 b, R = $-\text{C}(\text{CH}_3)_3$

under the same conditions was solvent sensitive. In methanol the product was exclusively 2,6-di-*t*-butyl-1,4-benzoquinone (IIb), (89.1 %), whereas in chloroform relatively smaller amounts of benzoquinone IIb (1.8 %), along with diphenobenzoquinone IIIb (7.8 %), were formed. Overall conversion in case of chloroform was poor (9.6 %). Higher selectivity towards benzoquinone in polar solvent can probably be explained on the basis of stabilization of a $\text{Co}^{\text{II}}\text{-O}_2$ complex in polar solvents (Stynes and Ibers 1972). However the similar reactivity of 2,6-dimethylphenol in chloroform and methanol in contrast to the marked difference of reactivity of 2,6-di-*t*-butylphenol in these solvents is not very clear at present.

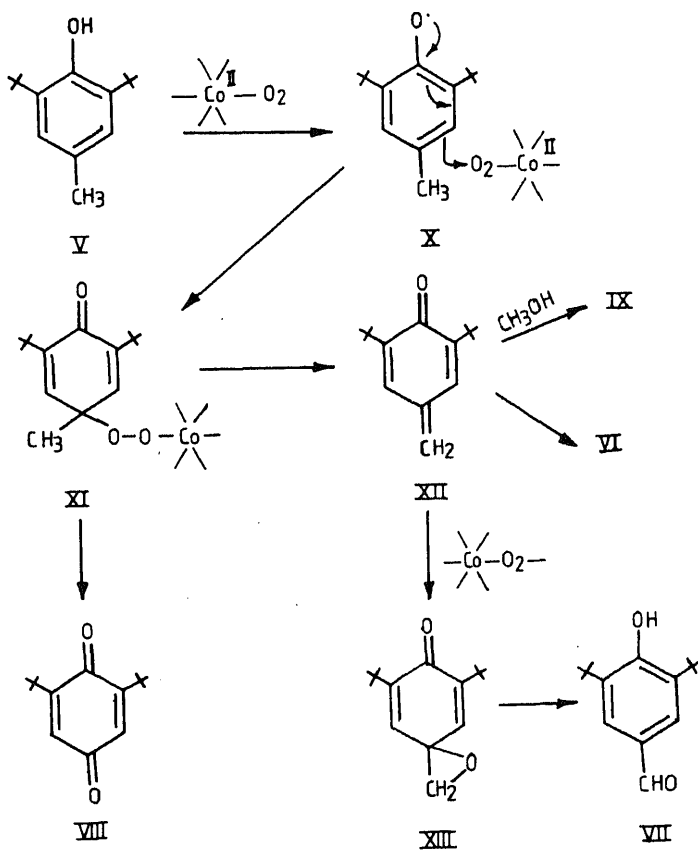
Oxidation of 2,6-di-*t*-butyl-4-methylphenol (V) showed significant differences in product distribution in chloroform and methanol (scheme 2). The products obtained in the oxidation of 2,6-di-*t*-butyl-4-methylphenol can be explained on the basis of a common intermediate phenoxide radical (X) (scheme 3). The radical X reacts with metal-dioxygen species to give peroxy quinolato- Co^{II} complex XI. The peroxy metal complex XI can either lose a methyl radical to form VIII or a hydrogen radical to form a quinone methide intermediate (XII). The intermediacy of quinone methide XII has been implicated in the oxidation of 4-substituted phenols by a variety of oxidizing agents (Gorbunova *et al* 1966; Magnusson 1966; Macomber 1982; Omura 1984). The quinone methide is trapped by methanol to give methyl ether IX in methanol and aldehyde VII presumably via XIII as shown in scheme 3. In a nonnucleophilic medium such as chloroform which is incapable of trapping it, the quinone methide forms a tail-tail dimer VI (Macomber 1982). For reasons not clear to us at present, methanol leads to products from both the intermediates XI and XII, whereas in chloroform only products derived from quinone methide are formed.

Our observations are in slight variance with the results reported earlier (Nishinaga *et al* 1974) that the oxidation of 2,6-di-*t*-butyl-4-methylphenol with $\text{Co}(\text{salen})$ in methanol gave rise to four products of which only two (VII and VIII) were obtained by us. They did not report the formation of methyl ether IX.

SCHEME 2



SCHEME 3



Oxidation of hydroquinone (**XIV**) with dioxygen in the presence of Co(salen)Py in chloroform gave 1,4-benzoquinone **XV** (40.7%) and quinhydrone **XVI** (35.2%) (scheme 4). Whereas oxidation of hydroquinone in methanol under similar conditions gave only polymeric material, van Dort and Geursen (1967) have reported similar results with a tetradentate cobalt complex, Co(salen) in the oxidation of hydroquinone. In contrast to this, oxidation of hydroquinone using Co[acacen-N,N'-ethylene bis(acetylacetoimine)] $2\text{H}_2\text{O}$ as catalyst in ethanol gave 1,4-benzoquinone, 64% (Mckillop and Ray 1977).

3. Experimental

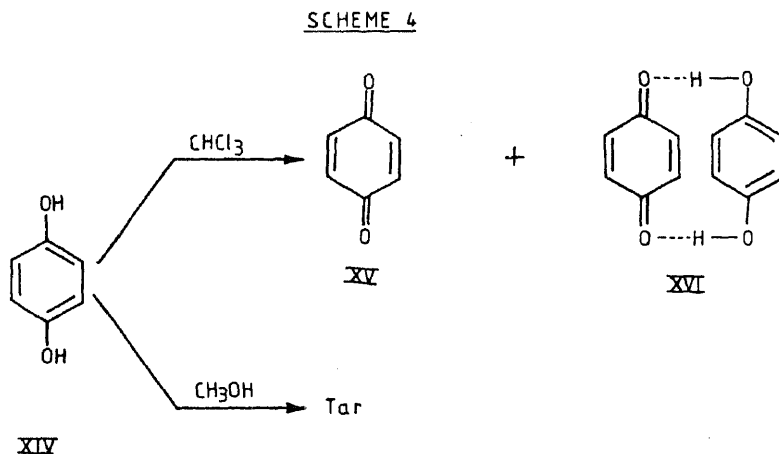
The m.p's are uncorrected; IR and NMR spectra were recorded on Perkin-Elmer 567 and Varian EM-360L, 60 MHz NMR spectrometer respectively. The NMR chemical shifts are in the δ scale. Yields refer to the pure isolated materials. All oxidation reactions were carried out in a tubular glass reactor provided with a gas inlet and outlet facility and a pressure gauge. The gas outlet was connected to a condenser and a solvent trap. Oxygen flow was controlled with the help of a stopcock fixed at the top of the condenser.

3.1 Materials

2,6-Dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone were used as supplied. Chloroform and methanol used were of high purity grade. Co(salen)Py was prepared by known methods (Bailes and Calvin 1947) and satisfactory elemental analysis was obtained. High purity oxygen gas from M/s Indian Oxygen Ltd. was used. Petroleum ether refers to the fraction b.p. 60–80°C.

3.2 Oxidation of 2,6-dimethylphenol

3.2a In chloroform: 2,6-Dimethylphenol (10 g, 82 m mole) was dissolved in chloroform (500 ml) and placed in the reactor. To it was added Co(salen)Py (1.65 g, 4.1 m mole) and oxygen was bubbled through the solution. Escaping oxygen was throttled in such a way



as to give a pressure of 1 kg/cm² g inside the reactor. After 6 hr, pressure was released and chloroform distilled off. The resulting mass was extracted with warm petroleum ether (2 × 100 ml). The petroleum ether extracts were evaporated to give an orange solid (7.0 g). The petroleum ether insoluble material was extracted with benzene (50 ml) and this on evaporation and drying gave a dark mass (2.2 g).

The orange solid obtained from petroleum ether extracts was crystallized from petroleum ether to give 2,6-dimethyl-1,4-benzoquinone (IIa) as orange needles (2.1 g, 18.8 %) m.p. 71–72°C (Mckillop and Ray 1977, m.p. 68–70°C). IR (KBr) 1640 cm⁻¹ (quinone). The mother liquor on concentration and cooling deposited biphenyl IVa as a grey solid (0.2 g, 2 %) m.p. 218–220°C (Tsuruya and Yonezawa 1974, m.p. 220–223°C). IR (KBr) 3350 cm⁻¹ (phenolic hydroxyl group); NMR (DMSO-D₆) 2.10 (12H, s, four methyls), 6.83 (4H, s, aromatic protons) and 7.87 (2H, s, hydroxyl protons); Mass *M*⁺ 242, 212, 165 and 121. The filtrate was concentrated and chromatographed over silica gel. Elution with petroleum ether gave more benzoquinone IIa (4.3 g, 38.6 %) and starting material (0.21 g, 2 %).

The benzene extracted material (2.2 g) was chromatographed over silica gel. Elution with benzene gave biphenyl IVa (0.2 g, 2 %) and diphenoquinone IIIa (0.1 g, 1 %) as red prisms from methylene chloride, m.p. 218–220°C (Mckillop and Ray 1977, m.p. 212–214°C). IR (KBr) 1625 cm⁻¹ (ketone) and 1580 cm⁻¹ (C=C).

3.2b *In methanol*: Oxidation of 2,6-dimethylphenol was carried out as above by using methanol as solvent in place of chloroform. Work up of the reaction mixture as mentioned earlier gave benzoquinone IIa (6.59 g, 59.1 %); diphenoquinone IIIa (0.4 g, 4.1 %); biphenyl IVa (0.37 g, 3.6 %); unreacted phenol Ia (0.75 g, 7.5 %) and tarry substance (1.1 g).

3.3 Oxidation of 2,6-di-*t*-butylphenol

3.3a *In chloroform*: To a solution of 2,6-di-*t*-butylphenol (10.3 g, 50 m mole) in chloroform (500 ml) was added Co(salen)Py (1.01 g, 2.5 m mole) and oxygen was bubbled through it at 1 kg/cm² g pressure for 6 hr. The reaction mixture was evaporated and the resultant brown mass extracted with warm petroleum ether (4 × 50 ml). Evaporation of the petroleum ether extracts gave brown oil which on crystallization from methanol gave dark brown needles of diphenoquinone IIIb (0.8 g, 7.8 %) m.p. 244° (Mckillop and Ray 1977, m.p. 243°C). IR (KBr) 1625 cm⁻¹ (ketone). The mother liquor was evaporated and the resultant brown oil was chromatographed over silica gel. Elution with petroleum ether gave benzoquinone IIB (0.2 g, 1.8 %) crystallized as orange needles from methanol, m.p. 63–65°C (Mckillop and Ray 1977, m.p. 60–62°C); IR (KBr) 1640 cm⁻¹ (quinone). Continued elution with petroleum ether gave starting phenol Ib.

3.3b *In methanol*: 2,6-Di-*t*-butylphenol (10.3 g, 50 m mole) was dissolved in methanol (500 ml) and to it added Co(salen)Py (1.01 g, 2.5 m mole). Oxygen was bubbled through the solution at 1 kg/cm² g pressure for 6 hr, after which pressure was released and the methanol evaporated. Residual mass was extracted with warm petroleum ether (4 × 50 ml). Evaporation of petroleum ether extracts gave an orange mass which crystallized from methanol to afford orange needles of 2,6-di-*t*-butyl-1,4-benzoquinone IIB (9.8 g, 89.1 %) m.p. 64–65°C.

3.4 Oxidation of 2,6-di-*t*-butyl-4-methylphenol

3.4a *In chloroform*: To a solution of 2,6-di-*t*-butyl-4-methylphenol **V** (10 g, 45.4 m mole) in chloroform (500 ml) was added Co(salen)Py (0.917 g, 2.27 m mole) and oxygen was bubbled at 1 kg/cm² g. After 6 hr, the pressure was released and chloroform distilled off. The residue was extracted with warm petroleum ether to remove the catalyst. Evaporation of the petroleum ether extracts gave a brown mass (10.7 g) which was chromatographed over silica gel. Elution with petroleum ether gave an oil which crystallized to give light yellow needles (from chloroform-methanol) of bibenzyl **VI** (2.82 g, 28.3%), m.p. 173–175°C (Paquette and Farley 1967, m.p. 169–170°C). IR (KBr) 3615 cm⁻¹ (hydroxyl group); NMR (CDCl₃) 1.45 (18H, s, *t*-butyl groups), 2.80 (4H, s, CH₂–CH₂–), 4.50 (2H, broad singlet, –OH) and 6.95 (4H, s, aromatic protons). Further elution with petroleum ether-benzene (95:5) gave 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (**VII**) (0.15 g, 1.4%) as colourless flakes (from methanol) m.p. 180–182°C (Paquette and Farley 1967, m.p. 186–188°C). IR (KBr) 1655 cm⁻¹ (aldehyde) and 3420 cm⁻¹ (phenolic OH); NMR (CDCl₃) 1.43 (18H, s, *t*-butyl groups), 2.67 (1H, s, –OH, exchangeable with D₂O), 6.47 (2H, s, aromatic protons) and 9.50 (1H, s, aldehyde proton). Continued elution with petroleum ether-benzene (95:5) gave starting material **V** (5.54 g, 55.4%)

3.4b *In methanol*: Oxidation of 2,6-di-*t*-butyl-4-methylphenol was similarly carried out using methanol in place of chloroform. Work up of the reaction mixture as above gave 2,6-di-*t*-butyl-1,4-benzoquinone **VIII** (2.73 g, 27.3%), m.p. 62–65°C, (Mckillop and Ray 1977, m.p. 60–62°C); 2,5-di-*t*-butyl-4-hydroxybenzaldehyde (**VII**) (0.39 g, 3.7%), m.p. 180–182°C and 2,6-*t*-butyl-4-methoxymethylphenol (**IX**) (3.1 g, 27.3%), m.p. 98°C, (Ronlan and Parker 1971, m.p. 98–99°C). NMR (CDCl₃) 1.45 (18H, s, *t*-butyl groups), 3.35 (3H, s, OCH₃), 4.30 (2H, s, –CH₂–O–), 5.23 (1H, s, –OH) and 7.03 (2H, s, aromatic protons); Mass *M*⁺ 250, 235, 219, 193 and 57.

3.5 Oxidation of hydroquinone

3.5a *In chloroform*: Hydroquinone (10 g, 91 m mole) dissolved in chloroform (500 ml) was placed in the reactor, Co(salen)Py (1.86 g, 4.6 m mole) was added and oxygen bubbled at 1 kg/cm² g for 6 hr. At the end of the reaction a dark brown mass precipitated out. It was collected, triturated with acetone (50 ml), and filtered. The acetone solution was concentrated and cooled, when it deposited greenish needles of quinhydrone (2.88 g, 29.1%), m.p. 170–171°C (Vogel 1978, m.p. 172°C). IR (KBr) 3220 cm⁻¹ (OH) and 1620 cm⁻¹ (quinone).

Chloroform filtrate of the reaction mixture was evaporated to give a black mass. It was extracted with boiling petroleum ether. The petroleum ether extracts on concentration deposited a black solid which was crystallised from acetone to give more quinhydrone (0.6 g, 6.1%). The mother liquor was further concentrated and cooled to give long yellow needles of 1,4-benzoquinone (4.0 g, 40.7%), m.p. 112–114°C (Mckillop and Ray 1977, m.p. 115°C). IR (KBr) 1650 cm⁻¹ (quinone).

4. Conclusion

The solvent has a marked effect on the nature and distribution of reaction products in the oxidation of substituted phenols using a Co(salen)Py-dioxygen complex under homogeneous conditions. Increase in the polarity of solvent enhances the stability of the Co(salen)Py-O₂ complex, resulting in higher yields of oxidised products (benzoquinones). Variation in product distribution in different phenols can also be ascribed to their structures.

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Reinvestigation of the antifungal activities of some aromatic N-oxides

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Abstract. Dinitroquinoline-N-oxide, 4-nitroquinoline N-oxide and a series of 4-substituted pyridine N-oxides have been subjected to MINDO/3 treatment in order to understand their antifungal activities. The photoelectron spectra and the nature of the N-oxide bond are discussed.

Keywords. Antifungal activities; MINDO/3 calculation; photoelectron spectra.

1. Introduction

The antifungal activities of 4-nitropyridine N-oxide, its 2-methyl derivative and 4-nitroquinoline N-oxide have been recognised long ago (Ochiai 1967). Experimental evidence also suggests that the presence of the nitro group in these N-oxides is essential for them to have any meaningful antifungal activity (Dodd and Stillman 1944).

The first attempt to correlate antifungal activity with nucleophilic superdelocalisability of the carbon [designated as C(4)] atom attached to the nitro group was due to Fukui *et al* (1960). Appreciating the ambiguity associated with the results of simple Huckel π -calculations, particularly for polar molecules like N-oxides, Kulkarni *et al* (1981) did all-valence calculations like the iterative extended Huckel (IEH) and MINDO/2 for these N-oxides. Their study could explain the electronic transitions, photoelectron spectral data etc. reasonably well, although it is rather inconclusive regarding the mechanism of the antifungal activity of the N-oxides. Moreover, the shortcomings of the MINDO/2 method have been realised by Bingham *et al* (1975) who have further improved upon this version of MINDO approximation to MINDO/3, which by all means is a superior SCF method.

With this background, it becomes essential that the findings of Kulkarni *et al* (1981) be assessed. It is thus necessary that we reinvestigate these N-oxides employing MINDO/3, whose results will obviously be more meaningful. One of the manifold purposes of this study is to understand why the presence of the nitro group is so vital to the antifungal activity of these N-oxides. For this purpose we have applied the MINDO/3 calculations to pyridine, pyridine-N-oxide, quinoline, quinoline-N-oxide,

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4-CN/OH/NH₂ pyridine-N-oxide and dinitroquinoline-N-oxide, in addition to 4-nitropyridine-N-oxide and 4-nitroquinoline-N-oxide which are proven antifungal compounds. It is also aimed at providing an insight into the mechanism of the antifungal activity of these compounds. In addition, the nature of the N-oxide bond has also been discussed.

The energies of occupied orbitals are also compared with the photoelectron spectral data, where available, to judge the reliability of the numerical values obtained from the MINDO/3 calculation. All the results of the present study are compared with the findings of earlier authors (Fukui *et al* 1960; Kulkarni *et al* 1981).

2. Method of calculation

The semi-empirical parameters for the MINDO/3 method were taken from Bingham *et al* (1975), without any modification. The structural parameters, where available, were taken from x-ray data (Eichhorn 1956; Ulku *et al* 1971) and otherwise, were transferred from related molecules. In the absence of optimisation, it was essential to keep the lengths of similar bonds, and the magnitudes of comparable angles, constant in all molecules, so that the change of electronic environment due to the variation of functional groups mainly influences the orbital energies.

3. Results and discussion

3.1 Photoelectron spectra and orbital energies

The ionisation energies obtained from MINDO/3 calculations are compared with the observed UV photoelectron spectral data in table 1.

The photoelectron (PE) spectra of pyridine-N-oxide and a number of substituted derivatives have been reported by Weiner and Lattman (1974) and by Maier and Muller (1974). These two reports, however, have provided different assignments for the first and second ionisation processes in pyridine-N-oxide. The PE band observed at 8.38 eV for this compound has been assigned (Weiner and Lattman 1974) to ionisation from the highest occupied σ -MO (mainly from oxygen), while Maier and Muller (1974) assigned this to the highest occupied π -MO. The results of the present investigation agree with Maier and Muller's view. This band (calcd. at 9.01 eV) corresponds to the highest occupied π -MO having a major contribution from the O-atom. It is interesting to note that like pyridine-N-oxide, in all its derivatives studied, the highest occupied molecular orbitals (HOMO) are of the π -type having a major contribution from the oxygen of the N-oxide moiety, with varying degrees of contribution from the ring atoms. The latter affect the HOMO energy substantially. However, for 4-NH₂ PNO, (PNO—pyridine-N-oxide), contributions from the N atom of the -NH₂ group and the oxygen of the N-oxide moiety are comparable; this factor has considerably lowered the energy of the HOMO for this molecule, compared to the others in this series. In most of these PNO compounds, a fairly invariant bond at $\approx$ 10.30 eV due to the π -electrons of the ring carbon atoms is obtained from the calculation. This band however, appears at 10.85 eV in 4 NO₂ ·PNO. The present assignments do not differ much from those of Kulkarni *et al* (1981).

Table 1. Ionization energies (eV).

Compound	Method	I_1^*	I_2	I_3	I_4
Pyridine	Obs.	9.26	10.50	12.27	13.0
	MINDO/3	8.54	9.18	9.81	10.39
		(σ)	(π^C)	(π^C, N)	(σ)
PNO**	Obs.	8.38	9.22	10.18	11.59
	MINDO/3	9.01	9.87	10.34	11.13
		(π^O)	(σ^O)	(π^C)	(σ)
4CN · PNO	Obs.	8.95	9.74	10.84	11.58
	MINDO/3	8.95	9.98	10.09	10.35
		(π^O)	(σ)	(σ)	(π^C)
4NO ₂ · PNO	Obs.	9.03	9.80	10.81	11.26
	MINDO/3	9.71	10.65	10.66	10.85
		(π^O)	(σ)	(σ)	(π^C)
4NH ₂ · PNO	MINDO/3	8.04	9.70	10.11	10.30
		(π^O, N)	(σ)	(π^C)	(π^N, O)
4OH · PNO	MINDO/3	8.55	9.87	10.33	11.20
		(π^O)	(σ)	(π^C)	(σ)
QNO**	MINDO/3	7.99	9.56	9.66	9.87
		(π^C, O)	(π^C)	(σ)	(π^O, C)
4NO ₂ · QNO	MINDO/3	3.52	9.72	9.91	10.07
		(π^C, O)	(σ)	(π^C)	(σ)

* I_i ($i = 1-4$) stands for the i th ionisation energy from MINDO/3 calculations;

** Pyridine-N-oxide is designated as PNO, and quinoline-N-oxide as QNO.

Table 2. Population of nitrogen and oxygen atoms in the N-oxide moiety.

Compounds*	Population							
	N				O			
	s	p_x	p_y	p_z	s	p_x	p_y	p_z
Pyridine	1.60	1.10	1.32	1.13				
PNO	1.30	0.99	1.00	1.05	1.94	1.70	1.17	1.84
4CN · PNO	1.27	0.99	0.98	1.03	1.92	1.68	1.24	1.79
4NO ₂ · PNO	1.27	0.99	0.98	0.99	1.92	1.69	1.24	1.77
4NH ₂ · PNO	1.27	0.98	0.98	1.09	1.92	1.68	1.23	1.83
4OH · PNO	1.27	0.99	0.98	1.09	1.92	1.67	1.23	1.82
QNO	1.30	0.99	0.97	1.04	1.92	1.73	1.21	1.77
4NO ₂ · QNO	1.30	0.99	0.98	0.97	1.91	1.71	1.27	1.71

* Abbreviations as in table 1.

3.2 Nature of the N-oxide bond

It is evident from table 2, that in all these N-oxides, the typical hybridisation on the

N-oxide moiety is more of a single bond than a double bond. This is in contrast to the earlier observation of Kulkarni *et al* (1981), where this bond was predicted to be fairly close to a double bond.

The mode of hybridisation of nitrogen ($s \approx 1.6$ $p \approx 2.41$) in pyridine however changes to $s \approx 1.3$ $p \approx 1.96$ in the pyridine-N-oxide. This may be traced to the higher electronegativity of the oxygen atom.

It is interesting to note that the 'NO' bond of the N-oxide moiety is different from that in an NO_2 group. In the latter the p_2 electrons are more delocalised to give the NO bond an appreciable π -bond character.

3.3 Antifungal activity

It has been suggested from experimental studies on these antifungal nitro-compounds that the mode of action involves interference with either a sulphydryl enzyme or the nitro-reduction system of the micro-organism (Fukui *et al* 1960). Amongst the compounds listed in table 3, 4-nitroquinoline-N-oxide has the highest antifungal activity followed by 4-nitropyridine-N-oxide. It is important to note that dinitroquinoline-N-oxide does not have the activity.

To answer the various questions associated with antifungal activity, a systematic examination of the effects of attaching an oxygen atom to the nitrogen of the ring, and also of introducing a nitro group at the fourth position in the ring, is of prime importance.

So far as the energy of the lowest unoccupied molecular orbital (LUMO) gives a measure of the electron accepting ability of these molecules, the simple N-oxides are better π -acceptors (and accordingly more reactive towards nucleophiles) than the parent compounds. Thus pyridine-N-oxide is more reactive towards nucleophiles as compared to pyridine (table 3). Also, on comparing the energy of the LUMO of pyridine,

Table 3. Energies* of HOMO and LUMO of substituted N-oxides.

Compound	Energy (eV)	
	HOMO	LUMO
Pyridine (Py)	-9.17	1.26
4NO ₂ ·Py	-9.90	-0.26
PNO	-9.01	0.45
4NO ₂ ·PNO	-9.71	-0.73
4CN·PNO	-8.95	0.18
4OH·PNO	-8.55	0.26
4NH ₂ ·PNO	-8.04	0.49
Quinoline	-8.16	0.23
QNO	-7.99	-0.14
4NO ₂ ·QNO	-8.52	-0.75
Dinitroquinoline-N-oxide	-8.91	-1.31

* For pyridine and 4NO₂·pyridine the HOMO are of the σ -type while they are of the π -type for the remaining compounds. However, for the sake of comparison, the energy of π -HOMO of these compounds are shown in the table. The LUMO on the other hand are all π -type.

pyridine-N-oxide and 4-nitropyridine, it is obvious that the introduction of a nitro-group at the C(4) position has made 4-nitropyridine a better electron acceptor than pyridine and pyridine-N-oxide. It is thus apparent that the combined effect of N-oxidation and introduction of a nitro-group at the C(4) position is to make the compound more reactive towards nucleophiles. Thus, 4-nitropyridine-N-oxide is the best π -acceptor amongst all the pyridine compounds listed in table 3. For the same reason 4-nitroquinoline-N-oxide is a better electron acceptor than quinoline and quinoline-N-oxide.

We now find a correlation between the ability to accept electrons and the antifungal activity. The two powerful antifungal agents, 4-nitroquinoline-N-oxide and 4-nitropyridine-N-oxide are good π -acceptors. The C(4) atoms in $4\text{-NO}_2 \cdot \text{PNO}$ and $4\text{-NO}_2 \cdot \text{QNO}$ —quinoline-N-oxide) have the highest frontier (LUMO) electron density amongst the C-atoms in the respective molecules and hence are the most probable sites for nucleophilic attack by the SH^- group. Of these two compounds $4\text{-NO}_2 \cdot \text{QNO}$ is a more potent antifungal agent than $4\text{-NO}_2 \cdot \text{PNO}$. Unfortunately, the energies of the LUMO of these compounds are quite comparable and hence not of much help in understanding their relative order of activity as antifungal agents. As optimisation of bond parameters was not carried out, the extent to which the energies of the LUMO can account for the relative order of activity remains indeterminate.

It is interesting to note that comparison of nucleophilic superdelocalizability of the C(4) atom in $4\text{-NO}_2 \cdot \text{PNO}$ and in $4\text{-NO}_2 \cdot \text{QNO}$ could not provide support to Fukui *et al* (1960).

Since the antifungal activities of these N-oxides appear to be due to their ability to accept electrons, one may wonder why dinitroquinoline-N-oxide, the most powerful electron acceptor in the series (table 3) does not show antifungal activity. The non-activity of dinitroquinoline-N-oxide may be traced to the fact that this compound, being an extremely powerful oxidising agent, gets destroyed before reaching the appropriate enzyme site.

4. Conclusion

In conclusion, it may be said that the antifungal activities of these nitro-aromatic N-oxides depend on their ability to act as good electron acceptors. The SH^- attacks the C(4) atom, which has the highest frontier electron density (LUMO) in the respective molecules. No simple relation between antifungal activity and superdelocalizability could be obtained.

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The identification and origin of N-H group overtone and combination bands in the near infrared spectra of 2-thiopyrrole-1,2-dicarboximides

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Abstract. Near infrared spectra ($4000\text{--}12\,000\text{ cm}^{-1}$) of 2-thiopyrrole-1,2-dicarboximide (TPH) and its N-deuterated analogue were measured in polycrystalline form at different temperatures between 410 K and 273 K. Spectra in solution were recorded as a function of concentration and temperature. The prominent bands so obtained could be interpreted in terms of overtone and combination bands of the N-H(D) and C=O groups modes. The results in CHCl_3 and CCl_4 solutions allowed differentiation between hydrogen bonded and non-hydrogen bonded bands. A comparison of cubic potential constant K_3 , mechanical anharmonicity $\omega_e x_e$ and electrical anharmonicity μ_2/μ_1 for the stretching bands indicates that these constants are not affected much by N-deuteration.

Keywords. Near IR spectra; combination modes; anharmonicity in N-H and C=O group vibrations: H-bonding in thiopyrroles.

1. Introduction

In view of the biological and medicinal uses of substituted pyrroles (Cotton *et al* 1964; Sindellari *et al* 1982) and the fact that a few of them form dimagnetic complexes with transition metals (Bosnich *et al* 1974; Saheb *et al* 1981), studies of the physical and chemical properties and their correlation with the vibrational and electronic spectra of these compounds have been of common interest. In this series we have reported the infrared vibrational analysis of the fundamental bands ($200\text{--}4000\text{ cm}^{-1}$) in a few thiopyrroles (Ram 1984; Ram *et al* 1984). The hydrogen bonding properties of the functional groups N-H and C=O along with the data on thermodynamic functions ΔH , ΔG and ΔS have been discussed therein. Singh and Agarwala (1979) and Saheb *et al* (1983) have reported dimagnetic complexes of similar molecules with transition metal ions in various oxidation states. Saheb *et al* (1983) and Saheb (1984) have also attempted the analysis of vibrational transitions (only fundamental modes) associated with the pyrrole ring and the *d-d* electronic transitions associated with transition metal ions.

The highly excited N-H group vibrations of pyrroles that fall in the near IR region have been shown to provide a better understanding of the hydrogen bonded molecular associations. This region of the spectrum is also important for physicochemical measurements and chemical analysis. In this paper we report the near IR

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(4000–12 000 cm^{-1}) spectra and thus the identity and origin of the characteristic bands of 2-thiopyrrole-1,2-dicarboximide (TPH) and its N-deuterated analogue (TPH-ND). Attempts have been made to clarify and evaluate the effects of the molecular associations on the character of the functional group vibrational modes.

2. Experimental

TPH was prepared by the method reported by Papadopoulos (1973) and was recrystallized in aqueous ethanol before use. The solvents CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 were of BDH reagent grade. N-deuterated TPH was obtained by refluxing a solution of TPH in D_2O for 10 hours. The process was repeated several times with fresh D_2O and the product was finally dried in a vacuum desiccator over P_2O_5 .

The IR spectra (200–4000 cm^{-1}) were recorded on a Perkin-Elmer-621 spectrophotometer using NaCl cells for solutions and KBr pellets ($\approx 1 \text{ mg}/200 \text{ mg KBr}$) for solid samples. Measurements in the near IR region (4000–12 000 cm^{-1}) were made on a Cary-17D spectrophotometer using quartz cells for solutions.

The temperatures at which spectra were recorded were varied and for solutions were maintained within $\pm 2 \text{ K}$ by circulating water through a water-bath, while for solid samples a Specac variable temperature cell using liquid nitrogen was used as the coolant. The reported frequencies are accurate to within $\pm 5 \text{ cm}^{-1}$.

3. Results and discussion

3.1 Fundamental absorption bands of N-H (D) and C=O groups of TPH and N-deuterated TPH

The spectral changes induced by the solvents and by N-deuteration are taken as the bases for the present assignments of the TPH bands in the near IR region. The IR bands which are potential contributors to this region are therefore established under the same condition of measurements. The data are summarised in table 1. As expected, the studies carried out in CCl_4 solution are more effective in the identification of hydrogen bonded and non-hydrogen bonded bands than those carried out in CHCl_3 solution because the former solvent permits a greater degree of self-association of the molecules.

The N-H and C=O stretching modes exhibit similar band structures giving rise to two/three different band components. The results in CH_3Cl and CH_2Cl_2 solutions are similar and do not give extra information over that in CHCl_3 solution. The intensities of the two band-groups at ≈ 3200 and $\approx 1750 \text{ cm}^{-1}$ are very sensitive to concentration. The band component at the highest frequency of each group is attributed to the free monomer, the middle one to intramolecular H-bonded (through O --- H bonding between $>\text{C}=\text{O}$ and $>\text{N}-\text{H}$ groups) monomer, and the third one to the intermolecular self-associated dimer of TPH (Ram 1984). These bands in N-deuterated TPH shift to lower frequencies by a factor ≈ 1.4 . The reliability of this assignment appears to be affirmed by both sets of experimental data and is further

Table 1. Prominent fundamental bands (in cm^{-1}) observed in the IR spectra of TPH and N-deuterated TPH as solids and in solution at room temperature (298 K).

TPH	Solid	CCl ₄ Solution (0.05 M)		CHCl ₃ Solution (0.50 M)		Assignment
	TPH-ND	TPH	TPH-ND	TPH	TPH-ND	
476 (32)	475 (33)	—	—	—	—	ν_{25} IP C=S bend
845 (12)	840 (8)	840 (120)	835 (110)	840 (100)	840 (90)	ν_{21} IP C=O bend
1122 (38)	1120 (35)	1135 (140)	1140 (130)	1120 (95)	1120 (70)	C=S stretch
1142 (64)	1141 (65)	1145 (500)	—	1145 (290)	1145 (280)	ν_{17}
1281 (28)	965 (15)	1296 (80)	960 (40)	1295 (70)	965 (60)	ν_{13} IP N-H(D) bend
1305 (58)	970 (45)	1310 (400)	975 (260)	1315 (200)	980 (150)	
1730 (45)	1735 (30)	1760 (100)	1760 (60)	1760 (75)	1765 (50)	ν_{5c} C=O stretch
1740 (51)	1745 (40)	1782 (440)	1778 (300)	—	—	ν_{5b}
1763 (58)	1765 (50)	1793 (600)	1785 (410)	1780 (300)	1780 (250)	ν_{5a}
3100 (16)	2320 (10)	3345 (40)	2510 (20)	3340 (13)	2510 (13)	ν_{1c} N-H(D) stretch
3150 (29)	2375 (15)	3410 (83)	2560 (30)	—	—	ν_{1b}
3200 (23)	2390 (20)	3440 (135)	2570 (120)	3430 (65)	2565 (80)	ν_{1a}

ν_i ($i = 1, 2, 3$ etc.) refers to vibrational mode number in the Mulliken (1955 scheme; *a*: Free monomer, *b*: intrabonded monomer, *c*: interbonded dimer, IP: in plane; the relative peak intensities (molar absorbance in solution spectra) are written in parentheses against the frequencies.

interest, i.e., the $\beta(\text{NH})$ and $\nu(\text{C}=\text{S})$ bands at ≈ 1300 and $\approx 1140 \text{ cm}^{-1}$, respectively, is consistent with the literature values (Lord and Miller 1942; Bellamy 1968).

3.2 Near infrared absorption bands of TPH and N-deuterated TPH

The near IR spectra of the two TPH comprise prominent combination and overtone bands of bonded and non-hydrogen bonded modes of N-H(D) and C=O groups. The H-bonded modes exert a greater influence on the character of the near IR spectrum than do the non-hydrogen bonded modes in any case. The band intensity and structure of a few H-bonded bands are modified drastically in going from solid to solution, and also within solutions of different concentrations in the same solvent. Figures 1 and 2 provide a comparison of these bands in TPH and N-deuterated TPH. The frequencies and relative band-intensities of the observed bands along with their proper assignment are summarized in table 2. The tentative assignments given here are based on the following: (i) the strong overtone/combination bands would arise primarily from the in plane-in plane oscillations of parent bands having appreciable intensities, whereas the weaker bands are expected to appear either from the in plane-out of plane oscillations of the $>\ddot{\text{N}}\text{-H(D)}$ and $>\text{C}=\ddot{\text{O}}$ groups (or of the TPH ring) or from the in plane-out of plane oscillations of the modes belonging to the cross species of these; (ii) the H-bonded bands would exhibit higher mechanical anharmonicity than the non-hydrogen bonded bands; (iii) the N-D bands in N-deuterated TPH would have relatively smaller mechanical anharmonicity than the N-H bands of TPH; (iv) while assigning an observed band to a suitable combination/overtone mode, an attempt is made to keep the mechanical anharmonicity to a minimum and of negative sign. In the following sections

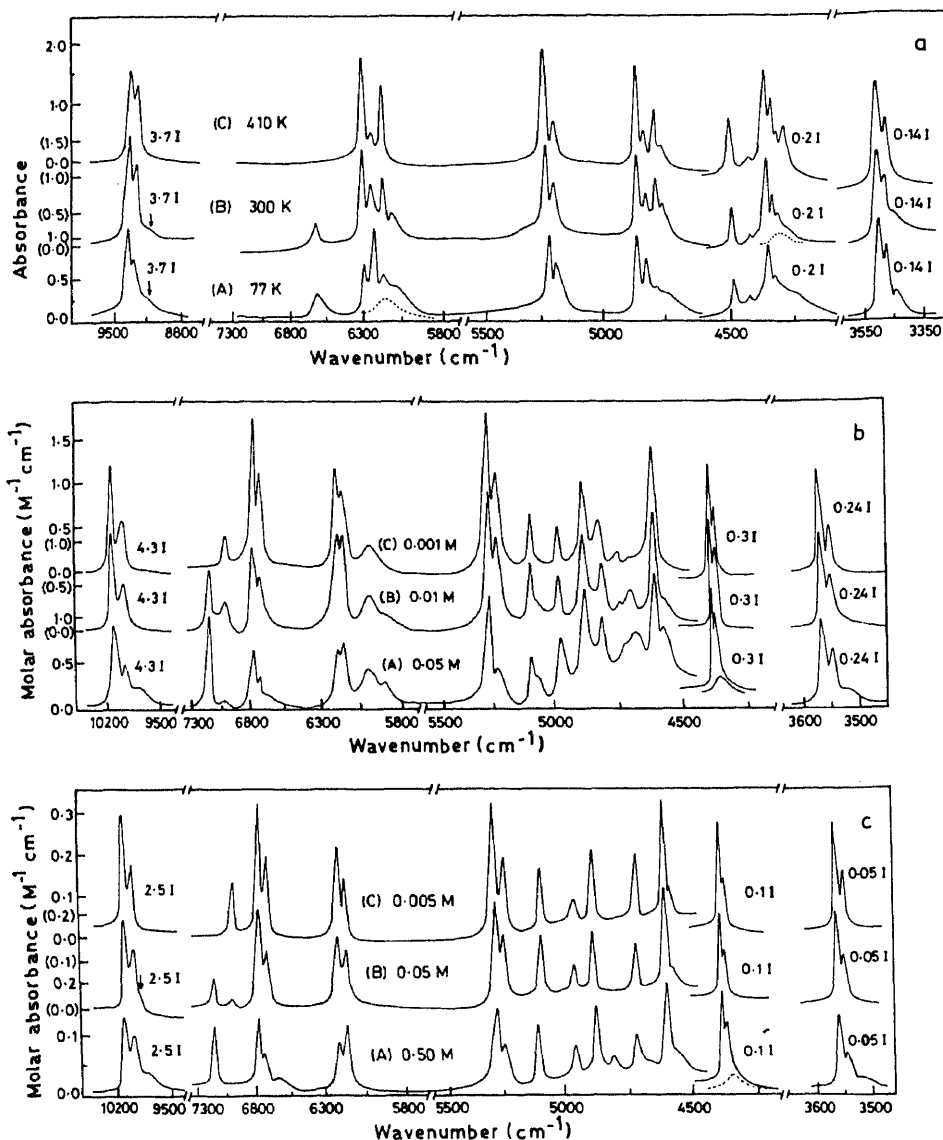


Figure 1a. The near IR absorption spectra of TPH at three different temperatures (A) 77 K, (B) 300 K and (C) 410 K. The dotted curves are the approximate contributions of the interbonded dimer bands (for discussion see the text). 0-14 I, 0-2 I and 3-7 I represent 0.14, 0.2 and 3.7 times intensity I (absorbance) respectively, given on the vertical axis. **b.** The near IR spectra of TPH corresponding to those of figure 1a in CCl_4 solution at three different concentrations (A) 0.05 M (B) 0.01 M and (C) 0.001 M (M: mole/litre). **c.** The near IR spectra of TPH corresponding to those of figure 1b in CHCl_3 solution at three different concentrations (A)

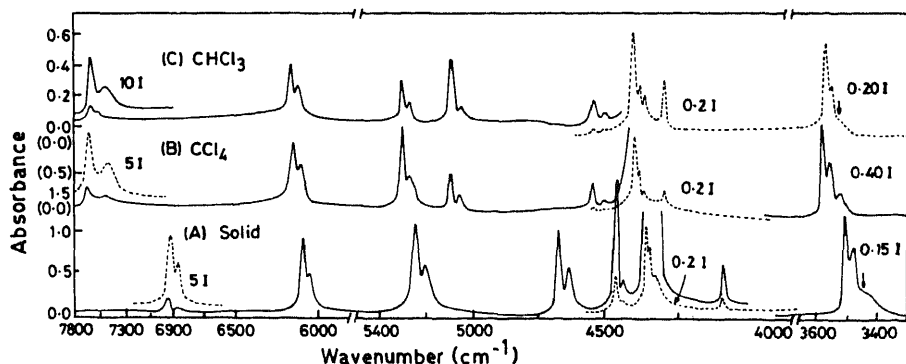


Figure 2. The near IR spectra of N-deuterated TPH in (A) solid, (B) CCl_4 solution (0.05 M) and (C) CHCl_3 solution (0.01 M). The solid and dotted curves represent the same spectra but at different intensity scales as is indicated.

3.2a N-H and N-D groups stretching bands: The N-H stretching vibrations of TPH in the fundamental mode show very little change with variations of temperature and concentration, but those in the overtone and combination bands differ drastically. The broad bands at ~ 6200 and $\sim 9200 \text{ cm}^{-1}$ in the solid sample comprise at least three different components. An advantage of measuring the spectrum between 77 and 410 K appears clearly in the 6200 cm^{-1} band. There is an intensity changeover in its three components at 6180, 6240 and 6295 cm^{-1} (values at 77 K) in going from 77 K to 410 K (see figure 1a). This may be due partly to a change of bonded $\rightleftharpoons$ non-bonded configuration and partly to a change of bandwidths leading to changed overlap conditions. The intensity of the latter two components increases with increase in temperature. These involve the $2\nu_{1a}$ and $2\nu_{1b}$ modes of TPH respectively. The 6180 cm^{-1} band is accordingly assigned to $3\nu_{5a} + \nu_{21}$. The dimer band $2\nu_{1c}$ does not appear at temperatures above $\approx 300 \text{ K}$. However, a considerably large and asymmetric spread (6000 to 6400 cm^{-1}) of the 6200 cm^{-1} band at $\approx 77 \text{ K}$ indicates its presence in a weak band centred at $\approx 6160 \text{ cm}^{-1}$. The corresponding second overtone bands likewise appear in the broad absorption at 9165 , 9285 and 9310 cm^{-1} , respectively.

We have also carried out these studies in different polar and nonpolar solvents to confirm the origin of these bands. Attempts are made to correlate predicted and observed changes in band positions due to IR band perturbations, or lack thereof, induced by changing the solvents. The $2\nu_1$ and $3\nu_1$ band positions remain almost the same in CHCl_3 and CCl_4 solutions showing a negative anharmonicity in $\omega_e \chi_e$ (a deviation from the predicted frequencies). The band intensity is modified, however, depending on the concentration of the solution and the nature of the solvent. In general, the bands are ≈ 5 times more intense in CCl_4 solution as compared to those in CHCl_3 solution. The molar absorbance ϵ ($\text{mol}^{-1} \text{ l cm}^{-1}$) in either solvent increases in non-hydrogen bonded bands (*a* species) and decreases in hydrogen-bonded bands (*b* and *c* species) as the concentration of TPH decreases. The combination bands at 6150 cm^{-1} and 6185 cm^{-1} (in CCl_4 solution) shift to higher frequencies (positive $\omega_e \chi_e$) with

Table 2. Prominent absorption bands observed in the near infrared spectra of TPH and N-deuterated TPH at room temperature (298 K).

Solid		CCl ₄ solution (0.05 M)		CHCl ₃ solution (0.5 M)		Assignment
ν (cm ⁻¹)	$\omega_e\chi_e$ (cm ⁻¹)	ν (cm ⁻¹)	$\omega_e\chi_e$ (cm ⁻¹)	ν (cm ⁻¹)	$\omega_e\chi_e$ (cm ⁻¹)	
2-Thiopyrrole-1,2-dicarboximide (TPH)						
3450 (20) } 3476 (65) } 3505 (90) }	-5 -2 -11	3520 (7) } 3548 (25) } 3568 (40) }	0 -8 -9	3518 (4) } 3542 (15) } 3555 (25) }	-1 — -3	2 ν_{5c} 2 ν_{5b} 2 ν_{5a}
4305 (10) } 4317 (26) } 4331 (35) }	+10 -4 -19	4366 (5) } 4380 (25) } 4395 (38) }	+6 -8 -13	4360 (2) } 4378 (10) } 4390 (18) }	-2 -4 -5	2 $\nu_{5c} + \nu_{21}$ 2 $\nu_{5b} + \nu_{21}$ 2 $\nu_{5a} + \nu_{21}$
4280 (16) } 4351 (60) }	+8 +9	4565 (5.5) } 4605 (13) }	+20 +20	4565 (0.5) } 4510 (1.9) }	— +35	$\nu_{1b} + \nu_{17}$ $\nu_{1a} + \nu_{17}$
4425 (7.0) } 4488 (28) }	-6 -17	4700 (4.0) } 4740 (5.5) }	-6 -10	— 4735 (0.8)	— -10	$\nu_{1b} + \nu_{13}$ $\nu_{1a} + \nu_{13}$
4758 (6.2) } 4780 (9.8) }	-11 -13	4810 (8.0) } 4875 (11.2) }	-34 -3	4810 (0.4) } 4870 (1.4) }	-27 0	2 $\nu_{5b} + \nu_{13}$ 2 $\nu_{5a} + \nu_{13}$
—	—	4980 (6.0) }	—	4955 (0.8) }	—	?
4825 (7.5) } 4880 (13) }	-75 -83	5075 (3.5) } 5118 (6.0) }	-117 -115	— 5115 (1.2)	— -95	$\nu_{1b} + \nu_{5b}$ $\nu_{1a} + \nu_{5a}$
5170 (8.5) } 5220 (14.5) }	-15 -13	5260 (4.5) } 5295 (12.5) }	-21 -19	5265 (1.0) } 5295 (1.6) }	-16 -13	3 ν_{5b} 3 ν_{5a}
—	—	5895 (3.0) }	—	—	—	$\nu_{1c} + 2\nu_{13}$
—	—	5975 (3.8) }	—	—	—	$\nu_{1b} + 2\nu_{13}$
—	—	6010 (4.5) }	—	—	—	$\nu_{1a} + 2\nu_{13}$
6094 (4.0) } 6180 (10) }	+59 +115	6150 (7.5) } 6185 (6.8) }	+50 +50	6150 (1.3) } 6190 (1.0) }	+45 +55	3 $\nu_{5b} + \nu_{21}$ 3 $\nu_{5a} + \nu_{21}$
6160* (2.0) } 6250 (9.0) }	-20 -25	6660 (1.8) } 6730 (3.5) }	-15 -45	6665 (0.3) } 6740 (0.8) }	-8 —	2 ν_{1c} 2 ν_{1b}
6305 (14.3) } —	-48 —	6780 (6.8) } 6975 (1.0) }	-50 -33	6780 (1.4) } —	-40 —	2 ν_{1a} 2 $\nu_{5a} + \nu_{1a}$
6640 (3.0) } 9125 (0.6) }	-85 -38	7140 (10.5) } 9760 (0.4) }	-70 -77	7130 (1.3) } 9810 (0.15) }	— -63	2 $\nu_{1b} + \nu_{25}$ 3 ν_{1c}
9295 (3.0) } 9380 (4.0) }	-27 -26	9935 (1.1) } 10105 (2.1) }	-53 -22	9970 (0.42) } 10105 (0.55) }	-47 -22	3 ν_{1b} 3 ν_{1a}
N-deuterated TPH						
3450 (20) } 3475 (60) }	-10 -8	3516 (3) } 3550 (20) }	-2 -3	3520 (5) } 3545 (15) }	-5 —	2 ν_{5c} 2 ν_{5b}
3505 (35) } 4130 (7) }	-13 -25	3578 (35) } 4310 (15) }	+4 -45	3568 (30) } 4310 (16) }	+4 -35	2 ν_{5a} $\nu_{1a} + \nu_{5a}$
4300 (22) } 4318 (40) }	+10 +3	4365 (15) } 4383 (35) }	+14 +2	4364 (13) } 4380 (16) }	+4 -5	2 $\nu_{5c} + \nu_{21}$ 2 $\nu_{5b} + \nu_{21}$
4330 (53) } 4440 (4) }	-15 +10	4400 (56) } 4500 (2) }	-13 -10	4405 (35) } 4508 (0.6) }	-3 -2	2 $\nu_{5a} + \nu_{21}$ 2 $\nu_{5b} + \nu_{13}$
4465 (18) } 4630 (6.5) }	-10 -60	4540 (3.5) } 5065 (3) }	-13 -27	4538 (1.7) } 5060 (1.0) }	-10 —	2 $\nu_{5a} + \nu_{13}$ 2 ν_{1b}
4670 (10.5) } 5210 (7) }	-55 -8	5100 (6) } 5270 (6) }	-20 -18	5110 (4.2) } 5275 (1.2) }	-10 -14	2 ν_{1a} 3 ν_{5b}
5230 (13) }	-9	5290 (13) }	-19	5318 (2.7) }	-11	3 ν_{5a}

spectra of simple aldehydes where C=O combination bands exhibit positive $\omega_e\chi_e$. In this agreement the 6150 and 6185 cm^{-1} bands can be correlated easily for the binary combination of $3\nu_{5b}$ and $3\nu_{5a}$, respectively, with ν_{21} (C=O bending). The features of the other bands of interest are as usual.

The spectra of N-deuterated TPH lack or show diminished intensity in most of the bands. The band groups at ≈ 4300 , ≈ 5200 and $\approx 6100 \text{ cm}^{-1}$ do not shift by N-deuteration. These bands therefore do not belong to N-H group modes. The observation of first and second overtone bands of N-D stretching modes in N-deuterated TPH at ≈ 4650 and $\approx 6400 \text{ cm}^{-1}$ in doublet structure (corresponding to *a* and *b* species) is concurrent with the absence of ≈ 6250 and $\approx 9200 \text{ cm}^{-1}$ bands in TPH upon conversion of N-H to N-D. The N-D stretching mode of interbonded dimer (*c* species) exhibits extremely poor intensity and hence could not be resolved in the present investigation for any combination or overtone band.

3.2b C=O group stretching bands: The C=O stretching modes of TPH as well as N-deuterated TPH are excited upto the third quanta. Intensity decreases continuously in successive excitations. As an example, the molar absorbences of monomer bands ν_{5a} , $2\nu_{5a}$ and $3\nu_{5a}$ in the CCl_4 solution of TPH are 600, 4.0 and 1.25, respectively. Corresponding values in the deuterated TPH are 410, 3.5 and 1.35, respectively. This shows the validity of the second order perturbation approach. Only the intensity of the second overtone band seems to be relatively higher. H-bonded bands *b* and *c* are more distinctly observed in the first overtone band at $\approx 3500 \text{ cm}^{-1}$. The spectral changes in these highly excited bands towards the effect of temperature, concentration and solvent vary in a fashion similar to the fundamental bands. A few binary and tertiary combination bands of C=O stretching modes that appear with the N-H group modes could be identified easily by N-deuteration (see table 2).

3.3 Anharmonicity in N-H(D) and C=O groups stretching modes

Our previous discussions reveal that the vibrational bands of N-H(D) and C=O groups of TPH may give valuable information about the involvement of these groups in the formation of hydrogen bonds. In this section we are interested in determining how the mechanical ($\omega_e\chi_e$) and electrical (μ_2/μ_1) anharmonicity parameters associated with these groups behave in the H-bonded and non-hydrogen bonded bands. The values for $\omega_e\chi_e$ were computed using second order perturbation formulae (Lucazeau and Sandorfy 1970), i.e.,

$$(\omega_e\chi_e)_{ii} = \nu_{i,01} - (\nu_{i,02})/2, \quad (1)$$

for the first overtone,

$$(\omega_e\chi_e)_{ii} = (\nu_{i,02})/2 - (\nu_{i,03})/3, \quad (2)$$

for the second overtone, and

$$(\omega_e\chi_e)_{ij} = \nu_{\text{comb}} - (\nu_{i,01} + \nu_{j,01}), \quad (3)$$

for the combination tones.

The symbols *i* and *j* represent the serial numbers of normal modes in the Mullikan (1955) notation. $\nu_{i,01}$, $\nu_{i,02}$ and $\nu_{i,03}$ are the frequencies measured on the cm^{-1} scale in

and electric dipole moment μ associated with a vibration of normal coordinates q are given by

$$V = \frac{1}{2} Kq^2 + K_3 q^3 + \dots, \quad (4)$$

$$\mu = \mu_0 + \mu_1 q + \mu_2 q^2 + \dots \quad (5)$$

If we neglect higher terms in (4), the cubic potential constant K_3 in terms of ω_e and $\omega_e \chi_e$ may be written as (Foldes and Sandorfy 1966).

$$K_3 = \pm 0.516(\omega_e |\omega_e \chi_e|)^{1/2}. \quad (6)$$

The positive sign is used when $\omega_e \chi_e$ is negative and vice versa.

A correlation of band intensities with frequencies (Herman and Shular 1954) in the fundamental and first overtone bands leads to

$$I_2/I_1 = [(\omega_2 - \omega)/(\omega_1 - \omega)] \{ \mu_1 b + \mu_2 / (\mu_1 - 5\mu_2 b) \}^2, \quad (7)$$

if

$$b = (k_3/\omega_e) \ll 1.$$

The observed intensity ratio I_2/I_1 (I_1 for the fundamental band and I_2 for its first overtone band) and calculated values of ω_e and b when substituted in the quadratic equation (7) give two different solutions of μ_2/μ_1 .

The $\omega_e \chi_e$ and μ_2/μ_1 values obtained using the observed band frequencies and intensities of the first overtone bands of the ν_1 and ν_5 vibrations are summarised in table 3. These could not be calculated for every H-bonded band as some of these are not

Table 3. The anharmonic constants $\omega_e \chi_e$, K_3 and μ_2/μ_1 as determined for the ν_1 and ν_5 modes of TPH and N-deuterated TPH in the approximation of the simple harmonic oscillator.

Vibration	$\omega_e \chi_e$ (cm ⁻¹)		K_3 (cm ⁻¹)		10 μ_2/μ_1	
	TPH	TPH-ND	TPH	TPH-ND	TPH	TPH-ND
<i>Solid sample</i>						
ν_{1a}	48	55	205.4	191.5	1.09, 2.54	0.82, -2.57
ν_{1b}	25	60	146.1	199.6	0.77, -1.75	0.65, -2.44
ν_{1c}	20	—	129.4	—	0.37, 1.22	—
ν_{5a}	11	13	72.4	78.8	2.26, -3.39	2.34, -3.60
ν_{5b}	2	8	30.5	61.2	2.29, -2.76	2.29, -3.26
ν_{5c}	5	10	40.2	68.4	1.19, -1.80	1.39, -2.30
<i>CCl₄ solution</i>						
ν_{1a}	50	20	217.3	118.0	-0.11, -1.14	-0.10, -0.92
ν_{1b}	45	27	205.0	137.1	-0.12, -1.06	0.18, -1.25
ν_{1c}	15	—	66.8	—	-0.28, -0.68	—
ν_{5a}	9	4	65.9	43.5	0.21, -0.95	0.41, -0.91
ν_{5b}	8	3	65.7	37.7	0.17, -0.91	0.36, -0.79
ν_{5c}	0	2	0	30.7	0.59, -0.59	0.64, -1.00
<i>CHCl₃ solution</i>						
ν_{1a}	40	10	139.5	82.1	-0.20, -0.89	-0.18, -0.83
ν_{1c}	8	—	84.6	—	-0.08, -0.60	—
ν_{5a}	3	4	30.8	43.5	0.47, -0.82	0.52, -1.03
ν_{5c}	1	5	37.6	48.6	0.30, -0.73	0.43, -0.99

The parameters for ν_{1b} and ν_{5b} bands could not be estimated in the CHCl₃ solution as these bands do not seem to appear in this solution.

well resolved in the fundamental modes or in the overtone modes. A comparison of the data in solid state as well in solution at different conditions of temperature and concentration indicates that $\omega_e\chi_e$ have lower values in the H-bonded bands. This observation seems in contrast to the general finding that H-bonding increases the magnitude of $\omega_e\chi_e$. It appears to us that the first overtone bands $2\nu_5$ couple strongly with the fundamental bands ν_1 as both lie in the $3100\text{--}3600\text{ cm}^{-1}$ region and satisfy the conditions of vibrational coupling (Varsanyi 1974). As a consequence, the frequencies of either band get modified showing no regular pattern for $\omega_e\chi_e$. In N-deuterated TPH, ν_1 (N-D stretching) bands shift to lower frequencies $2350\text{--}2600\text{ cm}^{-1}$, so that the coupling between these two modes becomes negligibly small. A relatively larger $\omega_e\chi_e$ value observed for a H-bonded band ν_{1b} in the deuterated TPH supports this fact (see table 3). The ν_5 mode has also the possibility of coupling with the C=C ring stretching vibrations. Perhaps due to this, the results of $\omega_e\chi_e$ for this vibration are not consistent even in the deuterated sample. It should be noted that the higher excited vibrations, $2\nu_1$, $3\nu_1$ and $3\nu_5$, are relatively free from vibrational mixing and their observed frequencies are more definite. The $\omega_e\chi_e$ derived using these band frequencies exhibit higher magnitude in H-bonded bands than in non-hydrogen bonded bands.

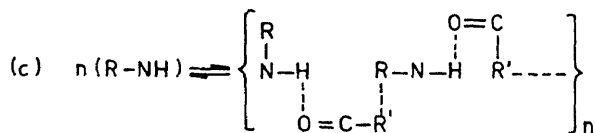
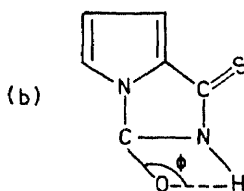
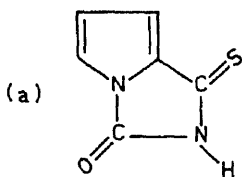
We now come to the effect of the N-deuteration of TPH. The $\omega_e\chi_e$ usually decreases except for the $2\nu_1$ and $2\nu_5$ bands in the solid state where its magnitude is larger in the deuterated sample. In fact, the vibrational frequency and the associated mechanical anharmonicity of a band depend largely on the local field and the symmetry of the concerned vibration site. In a pure gas phase system where the effect of nearest neighbours is minimum, the $\omega_e\chi_e$ of an X-D vibration is believed to have nearly one half the magnitude of the X-H vibration (Darling and Dennison 1940). However, in the solid state and in solution there seems no strict relation regarding their magnitudes. For example, the bending mode of water in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ exhibits the same $\omega_e\chi_e \approx 5\text{ cm}^{-1}$ (Srivastava *et al* 1976). These authors have also noted a few examples in which deuterated samples may have larger $\omega_e\chi_e$ than the undeuterated samples. Thus the results observed in this investigation (where $\omega_e\chi_e$ is similar in the two TPH for most of the cases) are not ambiguous. Moreover, ν_{1a} exhibits to ≈ 2.5 times lower $\omega_e\chi_e$ in CCl_4 solution and up to ≈ 4 times lower $\omega_e\chi_e$ in CHCl_3 solution. This indicates that both solvents offer almost similar environments for the TPH and N-deuterated TPH. The slightly lower values in the latter solvent may be attributed to a 1:1 complex between the sample and solvent molecules that may cause a shielding effect for vibrational coupling between favourable nearby vibrations (Nikolic *et al* 1983).

As compared to mechanical anharmonicity, the electrical anharmonicity parameter μ_2/μ_1 seems to be more sensitive to H-bonding. The origin of this parameter lies in the asymmetric variation of the effective charges during mechanical vibration in the system. In the N-H bond stretching ν_{1a} , the two atoms oscillate parallel to the N-H bond. Thus any change in the frequency of $\Delta\nu_{1a}$ in going from solid to solution would be associated with the asymmetric variation of the charges on either or on both the atoms. But μ_2/μ_1 shows no correlation with $\Delta\nu_{1a}$ ($\Delta\nu_{1a}$ exhibits almost the same value in CCl_4 as well as CHCl_3 solution while μ_2/μ_1 differs appreciably for the two solutions). So we conclude that the contribution of the charges on both atoms to the charge asymmetry is comparable. The absence of any systematic effect of N-deuteration also supports the view that the charge variation on H is less effective in the contribution to μ_2/μ_1 (if charge variations on H were the major contributors to μ_2/μ_1 , the effect would be less in

and the charges on the C and O atoms are equally responsible for μ_2/μ_1 . In the case of the interbonded polymer (figure 3c) the situation is a little different. The intensity of ν_{1c} (ν_{5c}) bands would appear mainly to be due to an asymmetric oscillation of the N-H . . . O=C bond groups (Ram *et al* 1984). The terms R and R' represent the parts of TPH excluding the N-H and the C=O groups respectively. The integer n can take values 2, 3, 4, . . . representing the dimer, trimer, tetramer etc. Thus bands of these associated polymers would be more sensitive in contributing to μ_2/μ_1 as compared to free monomer bands (totally symmetric). The values of μ_2/μ_1 listed in table 3 are also minimum for the ν_{1c} and ν_{5c} bands. This supports the above facts. On the other hand, for an intrabonded monomer system (figure 3b), the change in the dipole moment due to the O---H hydrogen bond during N-H/C=O oscillation would be at an angle ϕ between C=O and O---H bonds. ϕ usually takes values different from 180° . This means that the ν_{1b} or ν_{5b} bands would have less effect on μ_2/μ_1 . But this is not the observed case. What really happens is that the lone pair electrons on $>\ddot{\text{N}}\text{-H}$ and $>\text{C}=\ddot{\text{O}}$ groups are no longer localised on the parent atoms in the intrabonded system. These are shifted towards $>\ddot{\text{N}}\text{---H}$ and $\ddot{\text{O}}\text{---H}$ bonds causing a slight distortion in the N-H---O=C configuration so that it almost becomes a straight line. This is consistent with our present observation where ν_{1b} and ν_{5b} bands behave similar to the non hydrogen bonded bands ν_{1a} and ν_{5a} (the vibration is parallel to the bond extension).

4. Conclusion

The near IR spectra of 2-thiopyrrole-1,2-dicarboximides are dominated by the overtone and combination bands of N-H(D) and C=O stretching vibrations. The spectra in polar solvents, e.g., in CHCl_3 suffer a loss of intrabonded bands in fundamental modes and in a few combination bands. This indicates an intermolecular H-bonding between the solution and solvent molecules and the masking of the intra molecular H-bonded bands of the samples. The mechanical and electrical anharmonicity constants derived using the data to the first excited overtone bands have lower values in the H-bonded bands and do not show appreciable changes upon deuteration. In fact, the ν_5 , $2\nu_5$ and ν_1 vibrations are coupled strongly with nearby vibrations. The band position and



intensity of these bands, as a consequence, are modified and the results of $\omega_e\chi_e$ and μ_2/μ_1 calculated using these data are no longer of consistent trend for H-bonded bands. More accurate values of these parameters can be seen in the highly excited vibrations ($3\nu_1$ and $3\nu_5$ modes) where, as expected, the $\omega_e\chi_e$ exhibit greater values for H-bonded bands. Thus, a successful elucidation of the near IR bands which can be assigned uniquely to the bonded and non-hydrogen bonded modes of the imide group would permit possible utilization of a few well isolated overtone and combination bands for quantitative H-bonding studies in molecules having this group.

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Studies on I - V characteristics of dark and photoconduction in methylbixin

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Abstract. Dark and photoconductivities in methylbixin have been studied as a function of applied field and temperature. The results suggest that a single discrete trapping level is involved in charge carrier generation and the dominant trapping level is different for dark and photoconduction. Space charge limited current theory has been used to evaluate various transport parameters. The effective drift mobility is shown to be field dependent.

Keywords. Organic semiconductors; dark and photoconductivities; current-voltage characteristics; polyene semiconductors.

1. Introduction

Electrical conduction in biological compounds has been studied in the context of its playing a role in biological function (Kasha and Pullman 1962). The charge transport mechanism through these materials is, therefore, of much interest.

The variation of current through a sample with applied d.c. voltage is one of the easiest to measure and is also a very powerful technique for drawing conclusions about the characteristics of some transport parameters e.g. effective drift mobility of the carriers, density of trapping states, trap depth etc. The current voltage (I - V) characteristics are interpreted by considering the injection of space charge into an insulator by ohmic contacts. The non-ohmic behaviour in the I - V curves is the manifestation of the space charge limited current (SCLC).

We have measured dark and photo currents of methylbixin, a long chain polyene, as a function of temperature and field. The analysis of the I - V characteristics is made using SCLC theory. The results are interpreted in order to understand the charge transport mechanism and the dominant trapping level behaviour involved in methylbixin. In this paper, we present our results.

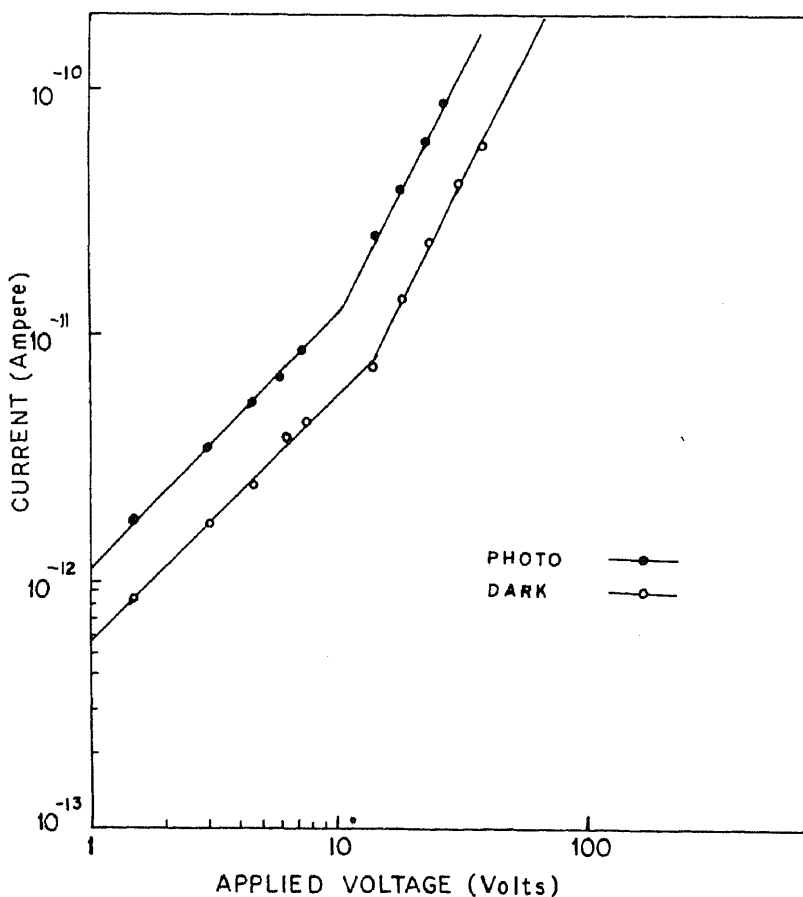
2. Experimental

The compound under investigation is a gift from the Hoffman-La Roche Co., Switzerland, and is used without further purification. The powdered sample was taken

in a sandwich cell with stainless steel and SnO_2 coated glass electrodes for conductivity measurements. The cell was placed in a suitably designed conductivity chamber (Mallick *et al* 1979) with a quartz window for photoconductivity studies. The applied d.c. voltage source were dry batteries. For current measurement, an electrometer (Model EA 815 of the Electronic Corporation of India Ltd.) was used. Temperature measurement was made using a copper constantan thermocouple attached at the top of the metal electrode. A high pressure 200 W mercury lamp was used for steady state photoconductivity work. Several measurements were made in order to ensure reproducibility of results both in vacuum and in an atmosphere of dry nitrogen. To get reproducible results, it was necessary to wait at least 45 minutes between changes in voltage to ensure that true equilibrium was attained.

3. Results and discussion

Figure 1 shows the I - V plots for methylbixin under dark and illuminated conditions at room temperature ($\approx 33^\circ\text{C}$). At high fields the square law behaviour is observed.



whereas currents at low fields are ohmic in nature. The cross-over field from ohmic to square law region is $\approx 2.68 \times 10^3$ V/cm for dark and $\approx 2.08 \times 10^3$ V/cm for photoconduction.

This square law behaviour may be interpreted in terms of either a single discrete trapping level or of exponential trap distribution.

For exponential distribution of traps, the current is given by (Rose *et al* 1955; Lampert *et al* 1964):

$$I = q\mu N_c VA/d [\epsilon_0 \epsilon V/qd^2 N_t(e)]^{(T_c/T)}, \quad (1)$$

whereas for a simple case of single discrete trapping level it is:

$$I = (9/8)\epsilon_0 \epsilon \mu [N_c/N_t(S)] A \exp(-E_s/kT) (V^2/d^3), \quad (2)$$

where q = electronic charge; μ = mobility; N_c = the effective density of states in the conduction band; V = applied voltage; d = interelectrode separation; A = area of the cell; ϵ_0 = free space permittivity; ϵ = dielectric constant; $N_t(e)$ = the total density of electronic levels in the exponential distribution; T_c = the characteristic temperature of the exponential trap distribution; T = working temperature in Kelvin; $N_t(S)$ = the density of trapping levels situated at an energy E_s below the conduction band edge and k : the Boltzmann constant. The quantity $[N_c/N_t(S)] \exp(-E_s/kT)$ is usually denoted by θ which is the ratio of free to trapped charges.

Equation (1) gives the square law dependence of I on applied voltage for $T = T_c$. Thus, the linear dependence of I on V^2 obtained at a constant temperature is insufficient evidence in favour of any particular type of trap distribution. From (1) and (2), we see that a plot of $\log_{10} I$ against $1/T$ should yield a straight line in both the cases and thus such a plot obtained at a single voltage does not remove the ambiguity in interpretation. However, the two types of trapping behaviour may be distinguished using measurements of the variation of current with temperature for a range of different constant voltages. For a single discrete trap level, the slope for such a plot is $[-(E_s/k)\log_{10} e]$ and is independent of applied voltage, whereas for exponential trap distribution the slope is $T_c \log_{10} [\epsilon_0 \epsilon V/qd^2 N_t(e)]$ which is voltage dependent.

We, therefore, studied the field dependence of the slopes from ohmic to SCL regions. A series of curves at different applied voltages as shown in figure 2 give a constant value of slope indicating the involvement of a single discrete dominant trapping level for photo and dark conduction.

We now proceed to evaluate some transport parameters involved in semi and photoconduction. The ohmic current (I_Ω) is given by

$$I_\Omega = n_0 q \mu (A/d) V, \quad (3)$$

where n_0 is thermally liberated free carrier density.

The onset of the SCLC injection takes place at cross-over voltage

$$V_t = (8/9) (qd^2 n_0 / \epsilon_0 \epsilon \theta), \quad (4)$$

which can alternately be written in terms of ohmic relaxation time $\tau = \epsilon/\sigma$ as,

$$V_t = (8/9) (d^2 / \mu_e \tau \epsilon_0) = (8/9) (d^2 \sigma / \mu_e \epsilon \epsilon_0), \quad (5)$$

where σ is the room temperature conductivity at the cross-over voltage and $\mu_e = (\mu \cdot \theta)$ is the effective drift mobility of the carriers. The above equations can be used to analyse the experimental I - V curves. The dielectric constant for β -carotene is 2.5 (Misra *et al*

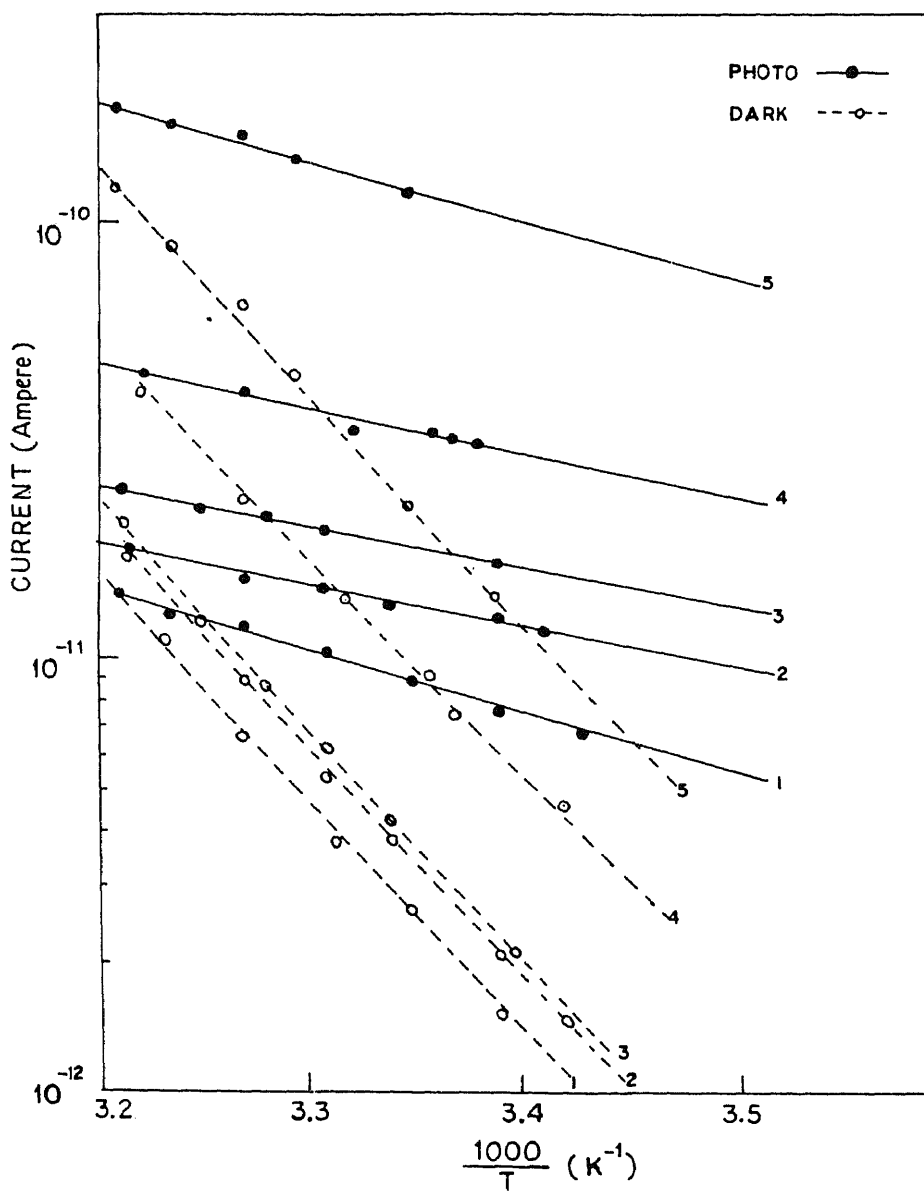


Figure 2. The plots of $\log I$ vs $1000/T$ at various applied voltages (1) 9 (2) 12 (3) 15 (4) 20 (5) 27 volts. The solid lines (—) represent dark and the broken lines (---) photoconductivity.

1968). We expect a similar value for methylbixin and we shall use this value for dielectric constant of methylbixin. The effective drift mobility may now be calculated

Table 1. Values of transport parameters.

Nature of conductivity	μ_e calculated from (2) ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$)	μ_e calculated from (5) ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$)	n_0/θ (cm^{-3} at 306 K)	E_t (eV)
Dark	7.74×10^{-8}	7.69×10^{-8}	3.1×10^{11}	0.99
Photo	2.14×10^{-7}	2.14×10^{-7}	2.42×10^{11}	0.20

is 'hopping' (Gutman and Lyons 1967). The enhancement in the effective mobility after illumination might be due to the change in θ . The different values of the slope for dark and photoconduction give the estimation of trap depths. For dark conduction it is 0.99 eV whereas it is 0.2 eV for photoconduction. The different values of trap depths are obtained due to the change in the charge carrier density and its distribution in different energy states and traps after illumination.

Information about the field dependent nature of the mobility can also be obtained by studying the I - V characteristics both in the dark and in illuminated conditions. If the non-ohmic behaviour of the dark current is due to the field dependence of mobility then the same behaviour is expected for photocurrents (Heilmier and Warfield 1963). Our results shown in figure 1 thus indicate the field dependence of mobility.

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Crystal spectra of methiodides of some nitrogen heteroaromatics

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Abstract. The longest wavelength bands of methiodides of some nitrogen heteroaromatics, which originate from a charge transfer (CT) transition, have been investigated in the solid state at liquid nitrogen temperature. The appearance of vibrational structure in the CT band has been established. Polarised crystal spectra have also been studied.

Keywords. CT band; vibrational structure; polarisation.

1. Introduction

Though charge transfer (CT) bands have been investigated extensively since 1952 some problems still remain unsolved. One of the problems is whether the multiplicity of a CT band occasionally observed is due to involvement of more than one donor (or acceptor) states or due to multiplicity of conformation. This problem has recently been discussed by us (Bagchi and Chowdhury 1979) with methiodide of diazenes as example, where we explained that the two CT bands $\approx 8000\text{ cm}^{-1}$ apart are due to multiplicity of donor final states in contradiction with the previous explanation that the two CT bands in methiodides of some pyridine derivatives are due to the presence of more than one acceptor level (Verhoven *et al* 1969; Mackay *et al* 1971; Kosower *et al* 1972). If close lying levels exist in both donor and acceptor, four bands instead of two should be observed. Since solution spectra are broad and featureless one way to study these is to increase the resolution by crystal spectra at low temperatures. Another reason for studying the crystal spectra is to resolve the vibronic contribution to CT bands, studies on which are relatively very few (Mulliken and Person 1969). Crystal spectra are also expected to yield polarisation of the CT band where again the controversy is not fully resolved. In the present work the CT absorption bands of the methiodides of pyrazine, pyridazine, quinaldine and acridine have been studied in the crystal state both at room and liquid N_2 temperatures.

2. Materials and methods

The amines were quaternised with methyl iodide and the compounds thus formed were purified by repeated crystallisation from dry ethanol. Crystals were grown from ethanol solution and polished by solvent. Some experiments were performed with identically oriented thin films of these compounds deposited on a quartz plate from ethanol

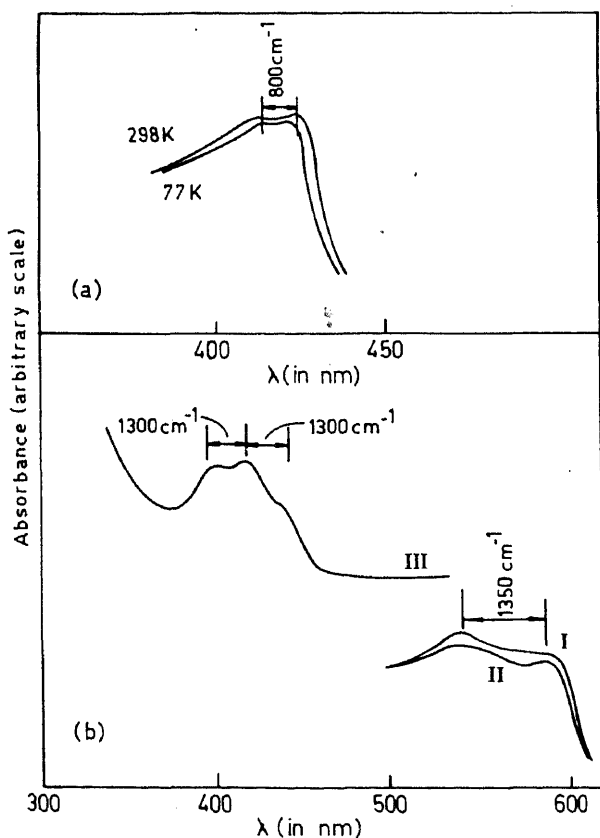
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solution. The experimental set-up for the measurement of absorption spectra of the crystals have been described previously (Bagchi and Chowdhury 1976). A cold finger type of Dewar was used for recording the spectra at low temperatures. A quartz Wallaston prism was used to polarise the light incident on the crystal (Bera *et al* 1969).

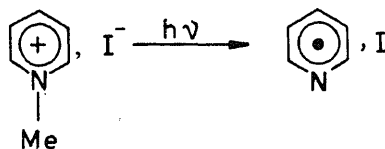
3. Results and discussion

The longest wavelength bands for the crystals at 77°K are shown in figure 1. The bands for these compounds are very similar to those observed in solutions (Bagchi and Chowdhury 1979). Absence of similar bands in the corresponding nitrate and perchlorate derivative indicate that the bands originate due to an interaction between the iodide and the organic cation.

The bands are broad even at 77°K although the width is slightly less than that observed in solution. In solution, a number of possible conformation may exist for such ion pair complexes and as such the bands are likely to be broad. But such a possibility is



unlikely in the solid state and thus multiple conformation has no role to play as regards the width of the band. Moreover, the bands are asymmetrical with greater breadth on the high frequency side. The facts are in conformity with the assignment of CT nature to these bands where the equilibrium distance between the donor and the acceptor in the excited state is different from that in the ground state (Mulliken and Person 1969). Thus, like in the solution spectra, this band in the crystals presumably originates due to a transfer of charge from the iodide ion to the organic cation:



3.1 Vibrational features

The longest wavelength bands of pyridazinium and acridinium iodide show structure [figure 1 (a) and (b)]. This may be either due to the presence of more than one electronic state (or configuration) of the complex in the solid state, or due to vibrational structure. It appears that the distribution of charge density in the cation (figure 2) may lead to more than one geometry of the complex. In the event that the band structures are due to the presence of more than one electronic state (or configuration), the relative polarisation of the components would have been different. Whereas in the case of vibronic interaction one expects similar relative polarisation for the components. Polarisation studies of acridinium methiodide (figure 3) supports the latter view (we have not been able to prepare a single crystal of pyridazine methiodide and as such

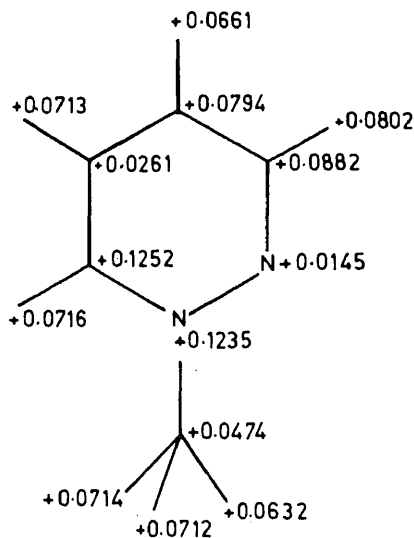


Figure 2. Distribution of charge densities in pyridazinium cation calculated by CNDO/2 method (Pople and Seegal 1966) using standard programme OCCE 29

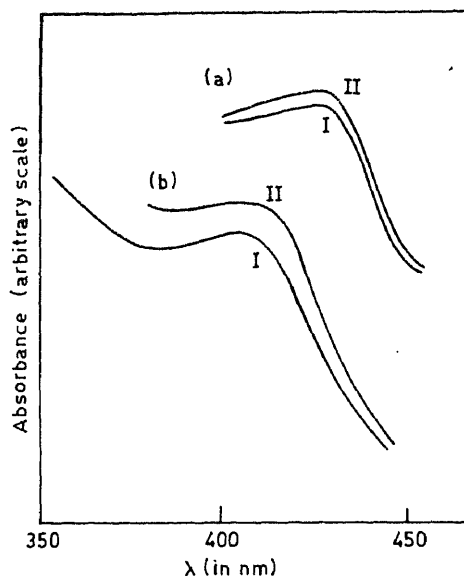


Figure 3. Polarised spectra of a single crystal of (a) pyrazine methiodide; (b) quinaldine methiodide (I = $e_{||}$ needle axis; II = $e_{\perp}$ needle axis).

no polarisation studies have been made for the compound). In fact the potential energy curve for ion-pair complexes has a deep, rather than a shallow minimum, and the vibrational characteristic of the excited state is very likely to appear in the crystal spectrum at low temperature. Another possibility that the appearance of such structures without distinct polarisation is due to any crystal field effect of the neighbouring ions, probably does not apply because this would demand the existence of a degeneracy in the energy levels of the donor and/or the acceptor in the absence of crystal field. We thus tentatively suggest that the lower energy band is the (O-O) band and the separation (800 cm^{-1} for pyridinium methiodide and 1350 cm^{-1} for acridinium methiodide) corresponds to excited state vibrational separation of the cation. It may also be pointed out that the vibrational structure observed in the crystal spectrum of the acridinium compound has close similarity to that observed in the solution spectrum ($\pi-\pi^*$ transition) of the corresponding cation. Thus it appears that during the process of charge transfer the electron goes to a π centre rather than to a localised centre of the cation.

3.2 Polarisation

The polarised spectra of the single crystals of the methiodides of pyrazine, acridine and quinaldine are shown in figure 3. For 1-1 complexes the theory predicts that the CT band should be polarised along the line joining the I^- ion and the centre of charge of

the planar cation lie roughly on a plane, the planar cations forming an endless column along the *a* axis. Unfortunately, the σ band of the ethyl derivative overlaps the π - π^* band of the cation and as such could not be studied. The σ band of the methyl derivative appears at a longer wavelength permitting the polarisation to be studied. The methyl derivative may be assumed to have the same crystalline structure. It is expected that the spectrum of the *bc* but not the *ab* plane should show sharp polarisation. We worked with thin films grown from solutions where we could only locate the *b* axis which coincides with the needles axis. The spectrum hardly shows any polarisation effect. The desired plane was probably not obtained. Further work on similar crystals at still lower temperatures is being planned.

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Simple equations for predicting volume properties of aqueous concentrated electrolyte mixtures*

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Abstract. Simple equations are presented for predicting density, compressibility and expansivity of aqueous mixed electrolyte solutions. These equations do not require any empirical parameter. Equations are tested upto very concentrated solutions and at various temperatures. It is essential to know the properties of single electrolyte solutions for predicting properties in mixtures. Predicted properties are in excellent agreement with experimental data.

Keywords. Volume properties; density; compressibility; expansivity; aqueous mixed electrolytes.

1. Introduction

Recently, there has been a continuous growing interest in the pvt properties of aqueous mixed electrolytes. The specific interaction theory of Pitzer (1973) was recently applied (Kumar *et al* 1982; Kumar and Atkinson 1983; Kumar 1985a, b) for estimating volume properties of aqueous electrolyte mixtures in the high ionic strength range. In addition, the Brønsted-Guggenheim theory (Guggenheim and Turgeon 1955) was used to develop suitable expressions (Kumar 1984a, b, 1985c) for evaluating pvt properties in dilute mixtures of electrolytes. These methods needed adjustable parameters mostly derived from constituent electrolyte solutions and a few derived from the mixtures.

In the following, equations are derived for estimating densities, compressibilities and expansivities of aqueous concentrated mixed electrolyte systems using the properties of single electrolyte solutions.

2. Equations

2.1 Density

Apparent molal volume ϕ_v of single electrolyte in water is given by (Millero 1972)

$$\phi_v = [1000(d_0 - d)/mdd_0] + (M/d), \quad (1)$$

where d and d_0 are densities of solution and pure water. M is molecular weight of electrolyte and m is molality.

* NCL communication No. 3825.

Similarly, mean apparent molal volumes of mixture of J salts is written as (Kumar 1984a):

$$\phi_V^* = \left[1000 (d_0 - d_m) / \sum_J m_J d_m d_0 \right] + \left[\sum_J m_J M_J / d_m \sum_J m_J \right]. \quad (2)$$

As shown recently (Kumar *et al* 1982) ϕ_V^* can be defined as

$$\phi_V^* = \left(\sum_J m_J \phi_{VJ} \right) / \left(\sum_J m_J \right), \quad (3)$$

where m_J is molality of an electrolyte in mixture and ϕ_{VJ}^0 is apparent molal volume of single electrolyte at the ionic strength of mixture. Ionic strength I of mixture can be given as

$$I (\text{mol} \cdot \text{kg}^{-1}) = \frac{1}{2} \sum m_i z_i^2, \quad (4)$$

where z is charge on ion of electrolyte.

Equation (1) can be rewritten for the J th electrolyte as

$$\phi_{VJ}^0 = [1000 (d_0 - d_J^0)] / [m_J^0 d_J^0 d_0] + (M_J / d_J^0), \quad (5)$$

where m_J^0 is the molality of the J th electrolyte alone at the ionic strength of mixture and d_J^0 is the density of the J th electrolyte alone at the ionic strength of mixture.

Substituting (5) into (3), equating with (2) and solving for d_m gives

$$d_m = \left(1000 + \sum_J m_J M_J \right) / \left\{ (1000/d_0) \left[\sum_J y_J ((d_0/d_J^0) - 1) + 1 \right] + \sum_J (m_J M_J / d_J^0) \right\}. \quad (6)$$

In (6), y_J is ionic strength fraction of the J th salt and can be written as,

$$y_J = m_J / m_J^0. \quad (7)$$

Equation (6) can be used to estimate the density of the mixture. d_0 , density of pure water can be taken from any reliable compilation (e.g. Kell 1975). d_J^0 , density of a single electrolyte solution at the ionic strength of mixture is available in literature.

2.2 Compressibility

Apparent molal compressibility ϕ_K of a single electrolyte solution is given by (Kumar 1984b).

$$\phi_K = [1000 (\beta d_0 - \beta_0 d)] / (m d d_0) + (M/d). \quad (8)$$

where β and β_0 are the adiabatic compressibilities of electrolyte solution and water respectively. Similar to (2), one can write an equation for the mean apparent molal compressibility ϕ_K^* as (Kumar 1984b).

where β_m is the adiabatic compressibility of aqueous mixed electrolytes. Using an identical relationship for ϕ_K^* as done in (3) and (5) and solving for β_m yields

$$\beta_m = \left[d_m (1000 \sum_j y_j \beta_j^0 / d_j^0 + \sum_j \beta_j^0 m_j M_j / d_j^0) \right] / \left(1000 + \sum_j m_j M_j \right). \quad (10)$$

One can use (10) to estimate the adiabatic compressibility of aqueous mixed electrolyte solutions of J th electrolytes. The sound velocity, U , can then be obtained using Newton's relation as,

$$u = (1/\beta_m d_m)^{1/2}. \quad (11)$$

Analogous to (10), which is derived on a molal basis, one can easily derive the expression for calculating adiabatic compressibility from apparent molar compressibility, β_{cm} which is given as

$$\beta_{cm} = \sum_j (y_j' [d_0 \beta_{cj}^0 - d_{cj}^0 \beta_0]) + (d_m \beta_0 / d_0). \quad (12)$$

Equation (12) has y_j' as ionic strength fraction on molar basis, where I_c is defined as $\frac{1}{2} \sum c_i z_i^2$. β_{cj}^0 is adiabatic molar compressibility of individual electrolyte solution at the ionic strength of mixture. d_{cj}^0 is the density of a single electrolyte solution at the molar ionic strength of mixture.

2.3 Expansivity

Expansivity α of an electrolyte solution is given by (Millero 1979):

$$\alpha = -(1/d) (\partial d / \partial T)_p. \quad (13)$$

Following the derivation of compressibility, one can easily derive

$$\alpha_m = \left[d_m \left(1000 \sum_j y_j \alpha_j^0 / d_j^0 + \sum_j \alpha_j^0 m_j M_j / d_j^0 \right) \right] / \left(1000 + \sum_j m_j M_j \right), \quad (14)$$

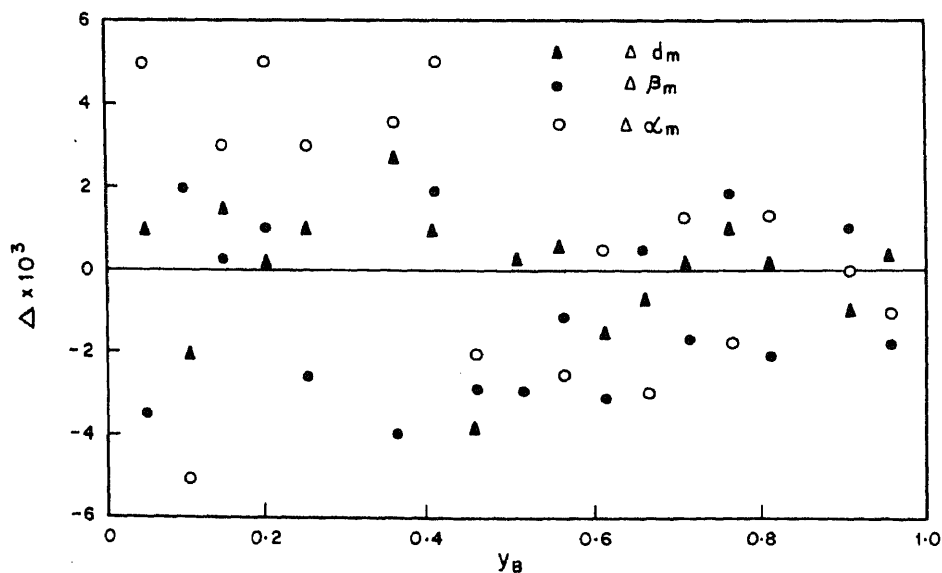
where the symbols have usual meanings and α_m is the expansivity of an aqueous mixed electrolyte solution.

3. Results and discussion

Equations (6), (10) and (14) can easily be used to estimate density, compressibility and expansivity respectively of aqueous mixed electrolyte solutions, provided the respective properties of single electrolyte solutions are known. Table 1 lists the various ternary, quaternary and multi-component systems analysed at various temperatures. Mixtures analysed contain systems with two different cations with a common anion, three different cations with a common anion, four different cations with a common anion, different cations and different anions, and associated electrolytes like sulphates and

Table 1. Summary of experimental data used for testing (6), (10) and (14).

Systems (aqueous)	t (°C)	σ Standard deviation (%)	References
<i>Density</i>			
NaCl-CaCl ₂	5-35	0.04	Kumar <i>et al</i> (1982)
			Kumar and Atkinson (1983)
CaCl ₂ -MgCl ₂	25	0.03	Kumar and Atkinson (1985a)
NaCl-MgCl ₂	25	0.015	Kumar and Atkinson (1985a)
NaCl-KBr	25	0.04	Kumar (1985b)
CaCl ₂ -ZnCl ₂	15	0.03	Huggins (1964)
KCl-KClO ₃	25, 50	0.04	Turnetskaya and Lepeshkov (1965)
CuSO ₄ -MgSO ₄	25	0.07	Turnetskaya and Lepeshkov (1965)
NaNO ₃ -Co(NO ₃) ₂	25	0.04	Avesina and Shevchuk (1967)
CsNO ₃ -Al(NO ₃) ₃	25	0.010	Aikhipov (1976)
Ca(NO ₃) ₂ -AgNO ₃	25	0.025	Khutsistova <i>et al</i> (1979)
NaCl-CaCl ₂ -MgCl ₂	25	0.029	Kumar and Atkinson (1985b)
NaCl-KCl-CaCl ₂ -MgCl ₂	25	0.035	Krumgalz and Millero (1982)
<i>Compressibility</i>			
NaCl-CaCl ₂	5-35	5.35×10^{-3} σ in sound speed = 0.12	Kumar <i>et al</i> (1982)
			Kumar and Atkinson (1983)
<i>Expansivity</i>			
NaCl-CaCl ₂	25	6.75×10^{-3}	Kumar and Atkinson (1983)

**Figure 1.** Experimental-calculated (Δ) density (d_m), compressibility (β_m) and expansivity (α_m) for NaCl-CaCl₂-H₂O at $I = 2$ and 25°C .

and calculated quantities (d_m , β_m and α_m) for a typical system aq. NaCl-CaCl₂ at ionic strength 2 and at 25°C. Experimental values were taken from the references listed in table 1. As clear from this figure, the difference Δ is random for all the properties. Statistically speaking, one can estimate the density, compressibility and expansivity to ± 0.03 , ± 0.005 and $\pm 0.006\%$ respectively which is good for most practical uses.

4. Conclusions

In the above approach, one can see that no empirical constants are used for prediction but yet the predictions are excellent. One can certainly estimate these properties with much higher accuracy though that is achieved by including various adjustable parameters as shown elsewhere (Kumar and Atkinson 1983).

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Excited state relaxation and energy transfer between $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ and $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$ in $\text{POCl}_3:\text{SnCl}_4$

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Abstract. Excited state relaxation in Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ aprotic solvent has been examined. It is found that at a concentration of 10^{-1} M Tb^{3+} , the fluorescence exclusively originates from the 5D_4 level. The appreciable increase in the decay times of Tb^{3+} in this solvent compared to its values in H_2O or D_2O , suggests that the decrease in non-radiative relaxations is due to the low energy vibrations characteristic of this solvent. Non-radiative transfer of energy from $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ and from $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$ in this solvent has been established by examining the lifetime data. Calculated values of energy transfer probabilities (P_{da}) in the liquid air temperature are analysed to obtain a clue regarding the nature of excitation transfer mechanism. In both the systems, the energy transfer from Tb^{3+} donors to Nd^{3+} as well as Ho^{3+} acceptors, occurs predominantly via a dipole-dipole process. At high temperature the energy transfer is increased.

Keywords. Excited state relaxation; energy transfer; fluorescence; Tb^{3+} donors; Nd^{3+} and Ho^{3+} acceptors.

1. Introduction

The luminescence of rare earths (RE) in solutions have been studied in less detail than in solids because of their low emission yields and shorter lifetimes. The main pathways for radiationless relaxations in the solid phase are the dissipation of excitation by multiphonon emission, concentration quenching (via cross relaxation) and quenching via a charge transfer state. In solutions containing rare earth ions the quantum yields and decaytimes of fluorescence is generally very low. Experimental studies on RE fluorescence have shown that when heavy water is substituted for ordinary water as solvent, both the fluorescence yield and decaytimes increase (Kropp and Windsor 1963, 1965, 1966; Pant *et al* 1971). Active rare earth ions in aqueous solutions undergo radiationless relaxations and the quantum yield of fluorescence are often low relative to the yields of the same ions in hydrogen-free solvents. Heller and coworkers (Heller 1966a, b; Lempicki and Heller 1966) have pointed out that the low quantum yields are by no means inherent in the nature of the liquid state. These relaxations result in part from the high energy vibrations of the bonds involving light atoms particularly hydrogen. The energy of stretching vibration between two atoms is a function of the inverse of the product of their masses. When this vibrational energy is of the order of the magnitude of the energy gap between the lowest excited state and the highest

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ground state of the rare earth ion, the excess energy may be lost by the excited ion. This loss of energy results in a radiationless relaxation. The higher the energy of the vibrational modes associated with the solvent, the lower is the fluorescence efficiency of the ion. The decrease in the RE fluorescence in water or organic (protic) solvents is attributed to the radiationless deexcitation via the overtones of O-H , >C-H , >N-H groups of solvent molecules both in the primary and secondary solvation sphere of the rare earth ion.

Earlier, spectroscopic studies of rare earth ions in liquid solutions at room temperature were mostly confined to the solvents containing hydrogen or deuterium atoms. Using the clue about the atomic masses playing a prominent role in reducing high frequency vibrations of the solvent, Heller (1968a, b) has solved the problem of creating efficient liquid laser by dissolving RE^{3+} in liquid systems which contain no atoms lighter than oxygen. Such liquids, free from hydrogen atoms, are called 'aprotic' solutions. Such systems have no vibrations of sufficient energy to carry away the energy difference corresponding to the gap between excited and ground multiplets levels of RE^{3+} . POCl_3 and SeOCl_2 mainly belong to this class which are used in combination with SnCl_4 , ZrCl_4 , SbCl_5 , AlCl_3 etc. to improve acidification so as to increase the solubility of RE salts. Depending upon the combination and composition of these solutions, remarkable enhancement in both the fluorescence and decay times of RE^{3+} in these heavy inorganic solvents is likely to occur.

For the luminescence studies of Tb^{3+} we have employed the $\text{POCl}_3 : \text{SnCl}_4$ aprotic solvent, which was used firstly by Blumenthal *et al* (1968), for room temperature liquid laser and recently by Chrysochoos and Takousbalides (1975, 1976). The Eu^{3+} emission in $\text{POCl}_3 : \text{SnCl}_4$ (5:1) has also been studied by Bhatt *et al* (1973). In this system POCl_3 molecules form the solvation shell around the RE^{3+} ion. The lightest atom in the shell is oxygen which is sixteen times heavier than hydrogen, as a consequence of which, the vibrational energies are likely to be about four times lower than that of hydrogen containing solvents.

Energy transfer processes between various rare earths in solutions have been studied to a limited extent. Holloway and Kestigian (1967) having studied the energy transfer from $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$, Ho^{3+} , Er^{3+} in water, came to the conclusion that the energy transfer mechanism was induced resonance. Antipenko and Ermolaev (1969) investigated the radiationless transfer of energy from Tb^{3+} and Eu^{3+} to various rare earth ions (including Nd^{3+} and Ho^{3+}) in acetone and water. A comparison of the rate constants of the transfer and the overlap integrals of the energy donor and acceptor spectra has proved that the transfer in acetone is accomplished by the exchange resonance mechanism, whereas in water, evidently exchange-resonance and induced-resonance transfer co-exist. Recently, the fluorescence enhancement of Eu^{3+} by Tb^{3+} in dimethylsulphoxide (DMSO) has been manifested by Chrysochoos (1974) who observed that the energy transfer process does not appear to take place via clear cut dipole-dipole interactions but rather via complex multipole and/or exchange interactions. Energy transfer between some rare earths in $\text{POCl}_3 : \text{SnCl}_4$ was reported for the first time by Antipenko *et al* (1970), who suggested that the transfer is accomplished

complexities of energy levels involved, the transfer mechanism in solutions is controversial. In the present investigation we wish to elucidate the transfer mechanism and character of multipolar transfer from Tb^{3+} donors to Nd^{3+} and Ho^{3+} acceptors in $\text{POCl}_3:\text{SnCl}_4$ aprotic solvent.

2. Experimental

The heavy inorganic solvent materials used in the study were POCl_3 (Analar grade, Albright and Wilson Ltd., England) and SnCl_4 (GR grade, E. Merck, AG, Darmstadt, Germany). Rare earth oxides Tb_2O_3 , Nd_2O_3 , Ho_2O_3 of 99.99 % purity were obtained from Indian Rare Earths Ltd., Kerala. These oxides were converted into chlorides by dissolving in Analard grade HCl and evaporating the solutions thus obtained in a low temperature oven.

The rare earth salts dissolve in POCl_3 to a limited extent, but they are fairly soluble when SnCl_4 is added, forming strong aprotic acid. For a solvent it is also necessary to have the transparency in the optical excitation and emission region of Tb^{3+} i.e. between 3000 Å and 8000 Å and this requirement is satisfactorily fulfilled by POCl_3 . The fluorescence efficiency of RE^{3+} is considerably affected by the ratio of $\text{POCl}_3/\text{SnCl}_4$. At low concentrations of SnCl_4 , rare earth salts are poorly soluble whereas at high concentrations of SnCl_4 , the complex $2\text{POCl}_3 \cdot \text{SnCl}_4$ is precipitated. Therefore, the variation in SnCl_4 has to be confined to within these two limits. In our system POCl_3 and SnCl_4 were, therefore, mixed in a ratio 9:1 by volume. The anhydrous rare earth chlorides were dissolved in this mixture in appropriate amounts in pyrex glass tubes of uniform bore and the solutions were quickly sealed in vacuum to avoid moisture. The Tb^{3+} concentration was kept fixed at 10^{-1} M and the activator (Nd^{3+} and Ho^{3+}) ion concentrations were varied in the range 10^{-3} M to 10^{-1} M.

Fluorescence spectra and decay times were measured in the usual manner. The emission spectra obtained in this study were not corrected with respect to the sensitivity of the phototube, because in taking ratios, such a factor will eventually cancel out. Measurements were made at room temperature (300°K), liquid air temperature (80°K) and high temperature (350°K).

3. Results and discussion

The fluorescence intensity distributions of Tb^{3+} (10^{-1} M) and Tb-Nd, Tb-Ho coactivated $\text{POCl}_3:\text{SnCl}_4$ (9:1 v/v) systems for various concentrations of Nd and Ho, are presented in figures 1 and 2 at room temperature (300°K). In these relative fluorescence measurements the geometry of the system was kept constant for all samples. The emission spectrum of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ shows four bands at 490 nm, 545 nm, 590 nm and 620 nm, which are assigned to the transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ respectively. The fluorescence of Tb^{3+} at this concentration (10^{-1} M) generally stems from the $^5\text{D}_4$ state similar to the emission of Tb^{3+} in aqueous, organic solvents as well as in DMSO whereas fluorescence of Tb^{3+} (10^{-2} M) in $\text{POCl}_3:\text{SnCl}_4$ arising from the $^5\text{D}_3$ state was observed for the first time by Takousbalides and Chrysochoos (1974), which has a strong dependence upon the

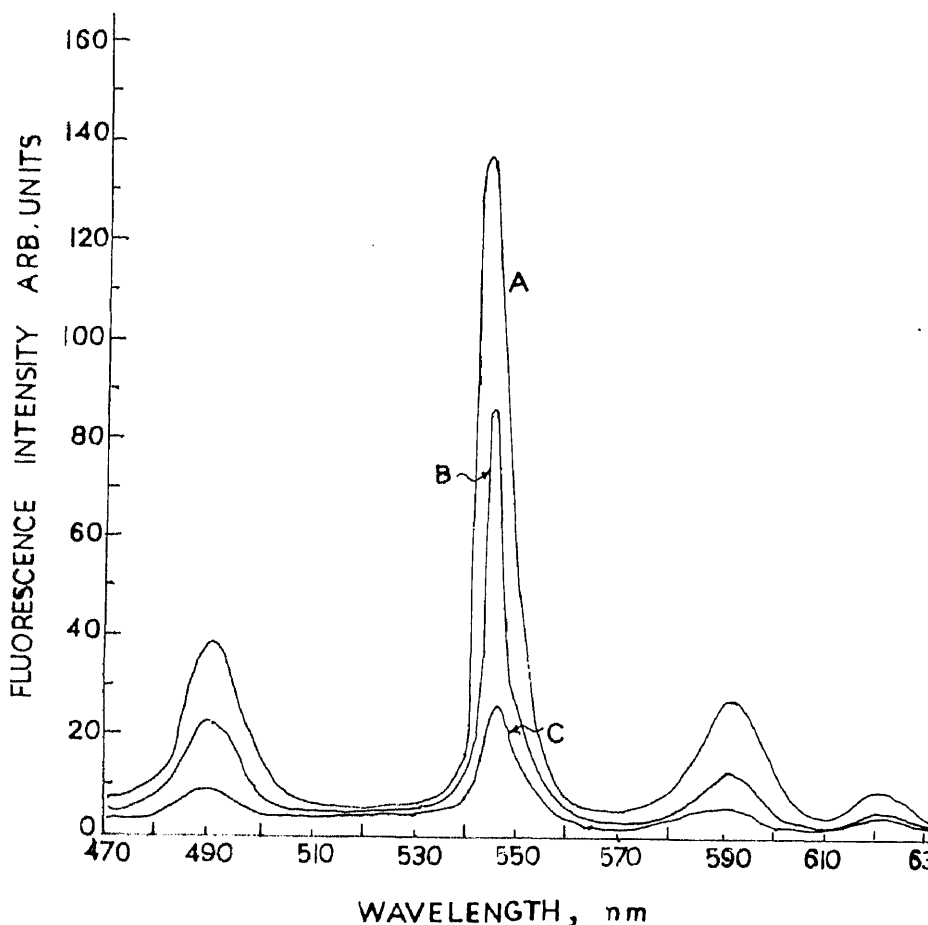
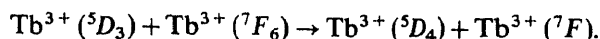


Figure 1. Fluorescence spectrum of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at 300°K with varying concentration of acceptor ions (Nd^{3+}): (A) Tb^{3+} (10^{-1} M) only; (B) Tb^{3+} (10^{-1} M) + Nd^{3+} (10^{-3} M); (C) Tb^{3+} (10^{-1} M) + Nd^{3+} (10^{-1} M).

emission from the 5D_3 state of Tb^{3+} , however, in our case could not be observed even at 80°K . The absence of this emission in our system is probably due to the fact that the Tb^{3+} concentration in our experiments is ten times higher than that of Takousbal and Chrysochoos. At these concentrations the luminescence quenching due to ion-ion relaxation can take place via the reaction:



This results in a cross-relaxation of the Tb^{3+} ion from the 5D_3 to 5D_4 state. The object in fixing a higher Tb concentration in our system is to avoid the participation of levels higher than 5D_4 , which make the transfer mechanism much complex. The Tb^{3+} fluorescence intensity is also increased due to feeding from upper levels, which is an added advantage.

Semilog plots of the typical decay curves of the transient fluorescence from 5D_3 and

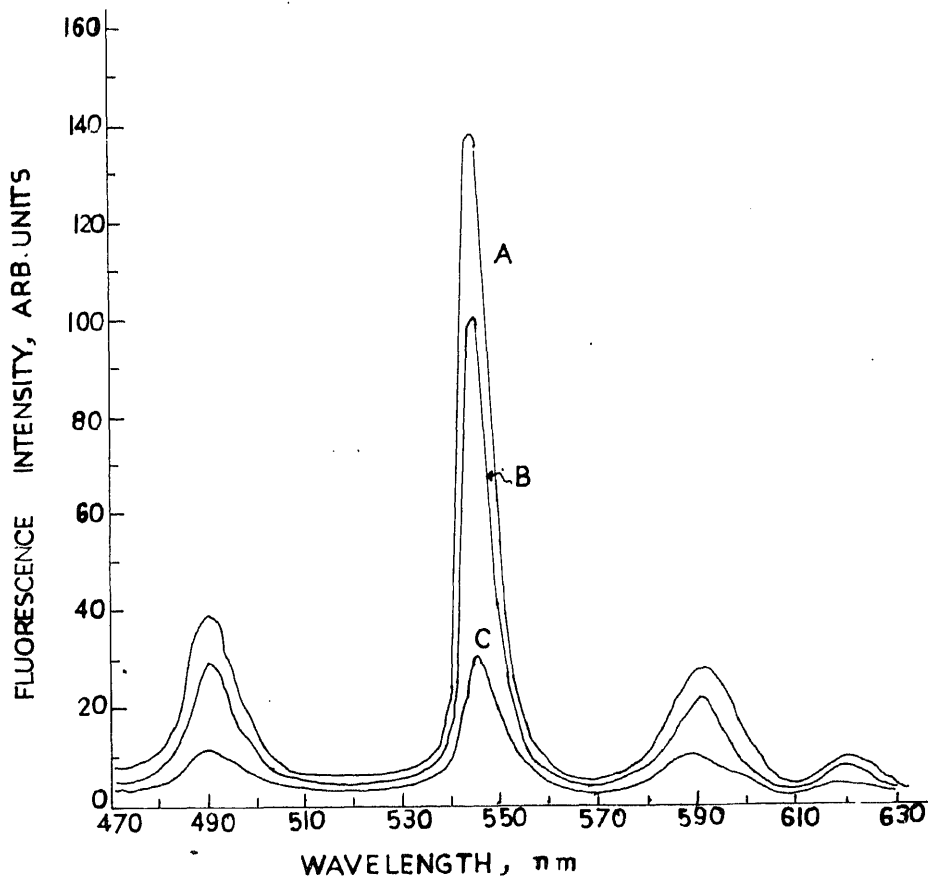


Figure 2. Fluorescence spectrum of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at 300°K with varying concentration of acceptor ions (Ho^{3+}); (A) Tb^{3+} (10^{-1} M) only; (B) Tb^{3+} (10^{-1} M) + Ho^{3+} (10^{-3} M); (C) Tb^{3+} (10^{-1} M) + Ho^{3+} (10^{-1} M).

of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ at room temperature (300°K) are illustrated in figures 3 and 4 at various concentrations of coactivators Nd^{3+} and Ho^{3+} respectively. The straight lines suggest that the fluorescence emitting state (5D_4) decays exponentially in pure Tb^{3+} as well as in the presence of Nd^{3+} and Ho^{3+} , contrary to the behaviour in glasses where the departure from exponentiality occurs in the early part of decay. This exponential behaviour is characteristic of the liquid state where due to Brownian motion the average distance between any two donors and acceptors remains constant whereas in glasses the distances between donor-acceptor pairs vary statistically. The pure exponential nature of the decay of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ in the Nd or Ho-free samples, as well as the homogeneously broadened emission bands are indicative of the fact that Tb^{3+} in this solvent has essentially one fluorescent site.

The fluorescence decay time of the 5D_4 level at room temperature was found in our system as $2800 \mu\text{sec}$, which is quite comparable to its values in glasses. Holloway and Harrison (1967) found that the decay time of Tb^{3+} in water solution is about $340 \mu\text{sec}$

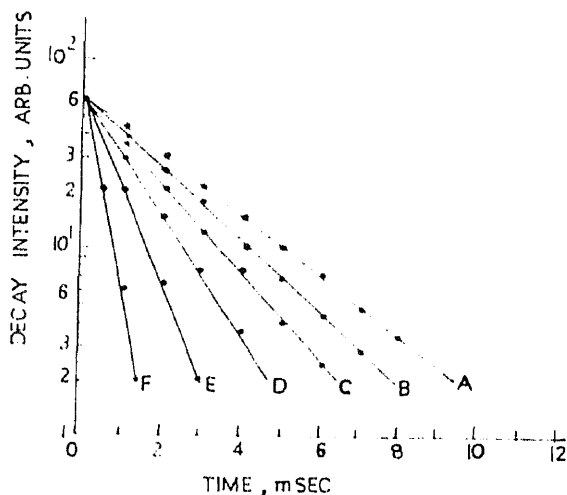


Figure 3. Semilogarithmic plot of the decay curve of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at various concentrations of Nd^{3+} (X), ($T = 300^\circ\text{K}$) where X is: (A) 0; (B) 10^{-3} M; (C) 5×10^{-3} M; (D) 10^{-2} M; (E) 5×10^{-2} M; and (F) 10^{-1} M.

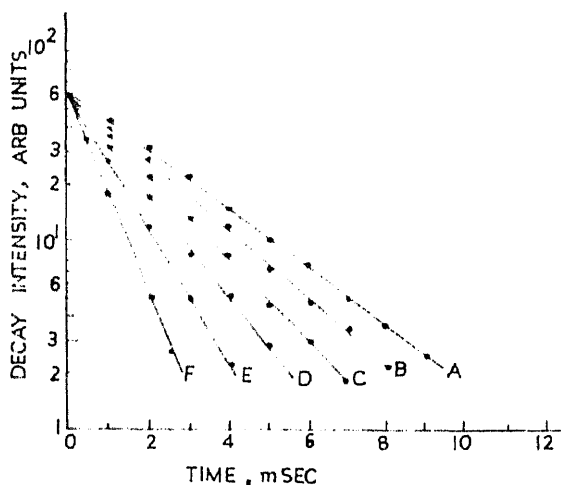


Figure 4. Semilogarithmic plot of Tb^{3+} (10^{-1} M) decay in $\text{POCl}_3:\text{SnCl}_4$ with various amounts (X) of co-activator (Ho^{3+}) ($T = 300^\circ\text{K}$) where X is: (A) 0; (B) 10^{-3} M; (C) 5×10^{-3} M; (D) 10^{-2} M, (E) 5×10^{-2} M, and (F) 10^{-1} M.

and that in D_2O is about $1200 \mu\text{sec}$. Our values of decaytimes in $\text{POCl}_3:\text{SnCl}_4$ are very much higher than those in H_2O or D_2O . Similar increase in the decaytimes and fluorescence intensities for various rare earths in aprotic solvents has been reported by Heller. Tokousbalides and Chrysochoos (1972) have also observed that both the fluorescence efficiencies and lifetimes of Sm^{3+} in $\text{POCl}_3:\text{SnCl}_4$ are enhanced about

relaxation processes result in the transformation of the excitation energy of the RE^{3+} ions into vibrational energy of the molecules of the solvent. The probability of such a process depends on the number of vibrational quanta that must be created in order to carry away the excitation energy of the ion. A process requiring the simultaneous creation of several quanta is highly unlikely. In cases where the available vibrational energy quantum is small compared to the excitation energy of the ion, a non-radiative energy relaxation will seldom take place e.g. in POCl_3 , where the highest energy vibrational quantum is 1300 cm^{-1} ; the stretching mode of >P=O group. On the other hand relaxation will take place more frequently when the available vibrational quantum is nearly equal to the excitation energy of the RE^{3+} ion. According to Siebrand and Williams (1968) the radiationless transition probability per unit time from Tb^{3+} to solvent vibrational modes is given by

$$W = (2\pi/\hbar) \cdot \beta^2 \cdot \rho \cdot F,$$

where β is the electronic transition matrix element (induced by vibronic interaction of solvent perturbations), F is the Franck-Condon factor and ρ is the effective density of the quasicontinuum formed by the solvent vibrations. Both ρ and F are greatly affected by the high frequency vibrations, making W appreciable, hence a low quantum yield will be observed in H_2O or D_2O . In $\text{POCl}_3:\text{SnCl}_4$ system, the absence of high frequency vibrations greatly reduce the density of the quasicontinuum formed by the solvent vibrations matched with the emitting state of Tb^{3+} . This reduces the non-radiative loss with the consequent enhancement in fluorescence yield.

The decaytimes of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ at the temperature 80°K , 300°K and 350°K with various concentrations of activators are presented in table 1. It is observed that in pure Tb^{3+} , the decaytime at room temperature is $2800\text{ }\mu\text{sec}$ which increases to $3200\text{ }\mu\text{sec}$ at liquid air temperature and decreases to $1600\text{ }\mu\text{sec}$ at 350°K . This strong temperature dependence of decaytime suggests that non-radiative processes largely decrease at liquid air temperature. A similar effect of temperature on intensity was also observed. It is inferred that with the increase in temperature there is a rapid increase in the temperature-dependent non-radiative rate constants, with the consequent decrease in decaytimes. Collisions of the second kind (Cario and Franck 1923) may also be effective in the quenching of Tb^{3+} fluorescence.

Table 1. Decaytimes of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ with varying acceptor concentrations and temperatures.

Acceptor concentration (mole)	Donor lifetime (m sec) in presence of acceptor (Nd^{3+})			Donor lifetime (m sec) in presence of acceptor (Ho^{3+})		
	80 K	300 K	350 K	80 K	300 K	350 K
0	3.2	2.8	1.4	3.2	2.8	1.4
10^{-3}	2.7	2.3	1.3	2.8	2.4	1.3
$5 \cdot 10^{-3}$	2.2	1.9	1.0	2.4	2.0	1.1
10^{-2}	1.7	1.4	0.7	2.0	1.6	0.8
$5 \cdot 10^{-2}$	1.1	0.9	0.5	1.4	1.2	0.6
10^{-1}	0.6	0.5	0.2	1.0	0.8	0.4

Donor (Tb^{3+}) concentration = 10^{-4} M (fixed)

In $\text{POCl}_3:\text{SnCl}_4$ absorption does not take place at the excitation wavelength (365 nm). Therefore, energy transfer from the solvent to the rare earths is ruled out. Further, the absorption spectra of this aprotic solvent appear (Chrysochoos and Tokousbalides 1973) at wavelengths shorter than 300 nm, hence the decrease in Tb fluorescence due to absorption by solution is also prohibited. Thus the overall reduction in the fluorescence of Tb^{3+} ion with increasing activator (Nd^{3+} and Ho^{3+}) concentration (figures 1 and 2) suggests that the non-radiative transfer of energy takes place from Tb^{3+} to Nd^{3+} and from Tb^{3+} to Ho^{3+} in $\text{POCl}_3:\text{SnCl}_4$. Further, the decrease in the decaytime of Tb^{3+} on increasing Nd^{3+} and Ho^{3+} contents at different temperatures (figures 3 and 4, table 1) support the non-radiative transfer of optical excitation. The electronic energy level diagrams of Tb^{3+} , Nd^{3+} , Ho^{3+} (presented in figure 5) have been reproduced after Dieke and Crosswhite (1963), because the energy level diagrams of RE^{3+} in crystals are also applicable to those in solution with the only difference that the pertinent absorption bands will be broader in the latter case. The excitation of 365 nm will populate the ($^5\text{G}_6$, $^5\text{L}_{10}$) excited levels of Tb^{3+} . The excited ion quickly relaxes to the $^5\text{D}_4$ metastable state, where the radiative transition is obtained at several ground multiplets. Energy transfer may take place from the $^5\text{D}_4$ levels of Tb

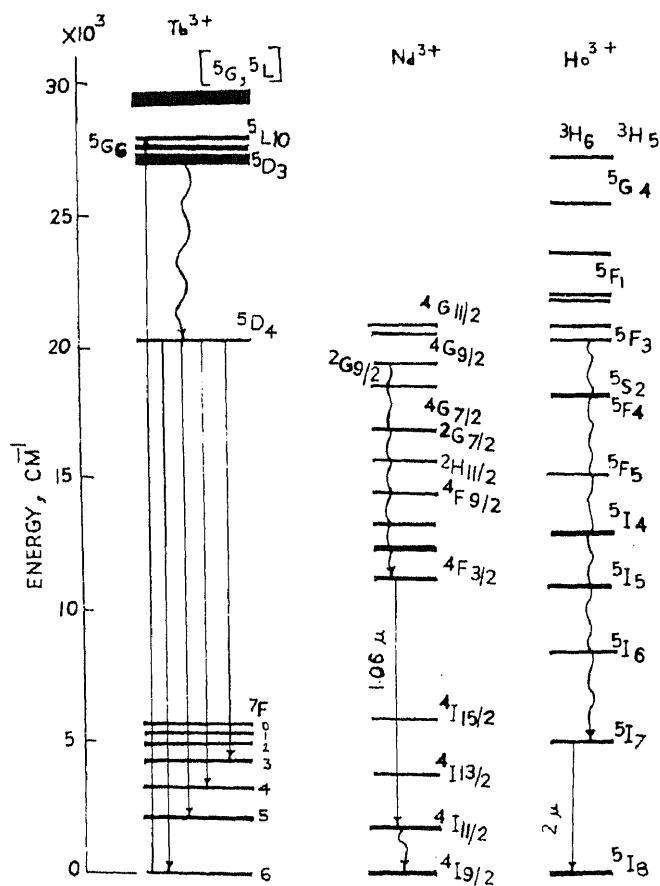


Figure 5. Energy level diagrams of Tb^{3+} , Nd^{3+} and Ho^{3+} .

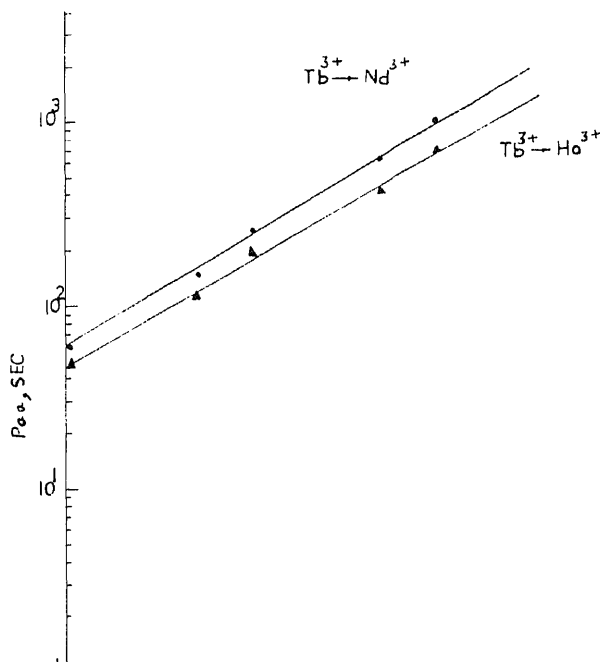
Table 2. Calculated values of energy transfer probabilities and efficiencies in $\text{POCl}_3\text{:SnCl}_4$.

Acceptor concentration (mole)	Energy transfer from $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$				Energy transfer from $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$					
	Transfer probability $P_{da} \cdot 10^3 \text{ sec}^{-1}$			Transfer efficiency η_T	Transfer probability $P_{da} \cdot 10^3 \text{ sec}^{-1}$			Transfer efficiency η_T		
	80 K	300 K	350 K	80 K	300 K	350 K	80 K	300 K	350 K	
10^{-3}	0.05	0.07	0.14	0.15	0.17	0.18	0.04	0.06	0.14	0.18
$5 \cdot 10^{-3}$	0.14	0.17	0.37	0.31	0.32	0.37	0.10	0.14	0.28	0.31
10^{-2}	0.27	0.35	0.80	0.47	0.50	0.56	0.18	0.26	0.62	0.50
$5 \cdot 10^{-2}$	0.59	0.75	1.37	0.65	0.67	0.68	0.40	0.47	1.04	0.62
10^{-1}	1.35	1.64	4.37	0.81	0.82	0.87	0.68	0.89	1.87	0.75

to several excited levels of Nd^{3+} as well as Ho^{3+} which are in resonance with Tb^{3+} transitions. Direct transfer from 5D_4 of Tb^{3+} may occur to $^4G_{9/2}$, $^4G_{5/2}$, $^2G_{7/2}$, $^2H_{11}$ levels of Nd^{3+} , which relaxes to the metastable $^4F_{3/2}$ level. Similarly in Tb^{3+} to Ho^{3+} energy transfer the various recipient levels of Ho^{3+} in resonance with the Tb^{3+} fluorescence are 5F_3 , 5S_2 , 5F_4 , which on direct transfer and rapid relaxation through sequence of intermediate levels may populate the 5I_7 metastable level of Ho^{3+} . The transitions from the $^4F_{3/2}$ level of Nd^{3+} and 5I_7 level of Ho^{3+} to their respective ground levels lying in the infrared region of the spectrum could not be detected as our measuring system was not sensitive in this region.

The energy transfer probabilities (P_{da}) and transfer efficiencies (η_T) were calculated using Reisfeld's formulae, frequently used in our earlier computations. The calculated values are presented in table 2.

As suggested earlier it is quite likely that at 350°K or 300°K, the collisions of solvent molecules may help in the energy transfer and a diffusion controlled process may be very effective, which in turn may make the transfer mechanism very complex (including exchange resonance mechanisms etc.). To avoid the undue interference of collisions the P_{da} data at 80°K (where diffusion-controlled processes are minimised) were analysed for the elucidation of precise transfer mechanisms. A plot of the calculated values of $\log P_{da}$ versus the log of acceptor concentration (figure 6) yields a straight line for both the systems $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ and $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$. The gradient of the curve is found



nearly equal to 2, which is the $\theta/3$ value from Van Uitert's formula, suggestive of a dipole-dipole mechanism of energy transfer from Tb^{3+} donors to Nd^{3+} and Ho^{3+} acceptors. The higher values of P_{da} for $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ transfer than for $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$ transfer, suggest that in the former system the transfer is more efficient than in the latter. This is further corroborated by a greater value of transfer efficiency (η_T) in the former compared to the latter, in accordance with the fact that the spectral overlap of Tb^{3+} emission with Nd^{3+} absorption is better than that with Ho^{3+} absorption.

Table 2 shows that transfer efficiencies as well as transfer probabilities increase with increase in temperature. In solid media such a phenomenon is attributed to the increased overlap of donor and acceptor levels due to thermal broadening, facilitating the broad path for energy transfer. However, in solution such a process may occur primarily due to collisional transfer. In $\text{POCl}_3:\text{SnCl}_4$ solvent the species POCl_2^+ and SnCl_4^{2-} are presumed to be generated which form a solvation sphere around the Tb^{3+} ion dissolving terbium chloride (Tokousbalides and Chrysochoos 1976). If a rigid solvation sphere around Tb^{3+} is established the quenching effect may be attained with the solvent molecules primarily located in such a sphere. Higher temperatures may partially destroy such a solvation sphere allowing penetration by solvent molecules from the secondary solvation sphere of the ion. As a consequence collisions will be increased and energy transfer will be enhanced. Such a process seems predominant at elevated temperatures.

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Determination of the number of *d* electron states in catalysts†

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Abstract. X-ray *K*-absorption edge measurements and metal Auger intensity ratios have been employed to determine the number of *d*-electron states in manganese oxide catalysts; the Auger method appears to be more reliable for the purpose.

Keywords. Manganese *K*-absorption edge; x-ray absorption edges of catalysts; Auger spectra of catalysts; *d*-electrons in catalysts.

1. Introduction

Metal Auger intensity ratios in transition metal compounds are determined by the number of valence electrons. Accordingly, the LVV/LMV Auger intensity ratio in first row transition metal compounds varies proportionally with the number of valence electrons (Rao *et al* 1980; Yashonath *et al* 1983). Metal Auger transitions can therefore be employed to investigate surface oxidation of metals. The number of valence electron states in transition metal compounds can also be determined by making x-ray absorption edge measurements since the chemical shifts of absorption edges are determined by the oxidation state or the effective charge of the metal (Sarode *et al* 1979; Sankar *et al* 1983). We considered it most worthwhile to carry out a comparative investigation of the *d*-electron states in MnO_2 and $\text{MnO}_2\text{-SiO}_2$ catalysts by employing both the Auger and x-ray absorption edge measurements. In the x-ray absorption edge study, we have employed the Mn ($1s \rightarrow 3d$) transition in the near edge structure besides the chemical shifts of the *K*-absorption edge.

2. Experimental

MnO_2 was prepared by the decomposition of the nitrate at 470 K in air. The sample of the $\text{MnO}_2\text{-SiO}_2$ catalyst (Mn content: 55 % (W/W)) was prepared by coprecipitation of MnO_2 and SiO_2 from an aqueous solution of KMnO_4 and sodium silicate using starch to reduce KMnO_4 from Mn^{7+} to a nominal Mn^{4+} . Both MnO_2 and $\text{MnO}_2\text{-SiO}_2$ samples were activated by heating in a stream of dry oxygen at 620 K for 3 hours. These catalysts were deactivated by heating them in air at 970 K. Reduction of the samples was carried out in dry hydrogen at 670 K for 3 hours. Mn metal, MnO , Mn_2O_3 , MnO_2 and KMnO_4 were studied as reference systems.

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X-ray induced Auger electron spectra (AES) were recorded with an ESCA III Mark 2 spectrometer of V.G. Scientific Ltd., U.K. *In situ* activation and reduction of the catalysts could be carried out in the sample preparation chamber of the spectrometer for the Auger studies. AES of these oxides have contributions from both inter and intra-atomic processes (Rao and Sarma 1982). For example, the L_{VV} transition of MnO would include $L(Mn)V(Mn)V(Mn)$ as well as $L(Mn)V(O)V(O)$ transitions. Since we were interested in the intra-atomic process, the interatomic contribution was subtracted out assuming the line shapes of the two transitions to be similar to those of the pure metal.

X-ray K -absorption spectra were recorded with a bent crystal spectrograph described earlier (Sankar *et al* 1983). The uncertainty in the measurement of the position was ± 0.8 eV. For the x-ray absorption measurements freshly prepared samples of known thickness were placed between cellophane adhesive tapes.

3. Results and discussion

3.1 X-ray absorption edge measurements

Typical x-ray absorption K -edge spectra of the various catalyst samples are shown in figure 1. Chemical shifts, ΔE , of the catalysts are tabulated in table 1 along with those of the reference manganese oxides. Chemical shifts of the reference manganese oxides increase progressively with the increase in the oxidation state of manganese or the decrease in the number of d -electrons. From figure 2 we see that the curve correlating

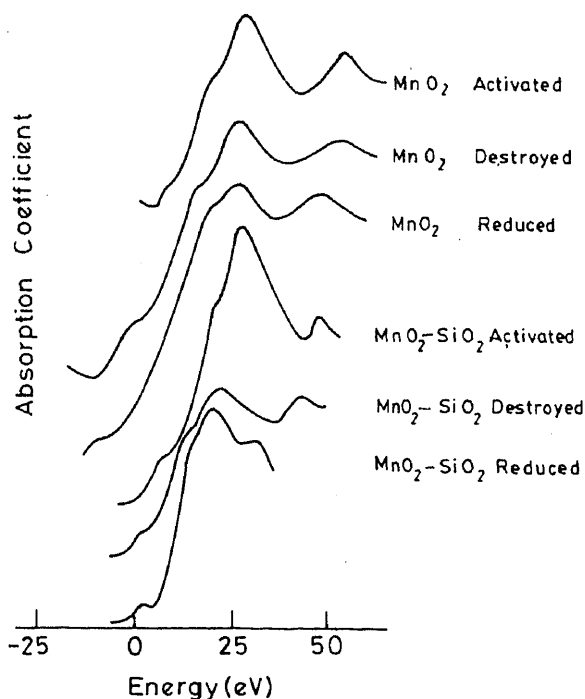


Figure 1. X-ray absorption K -edge spectra of MnO_2 and MnO_2-SiO_2 catalysts.

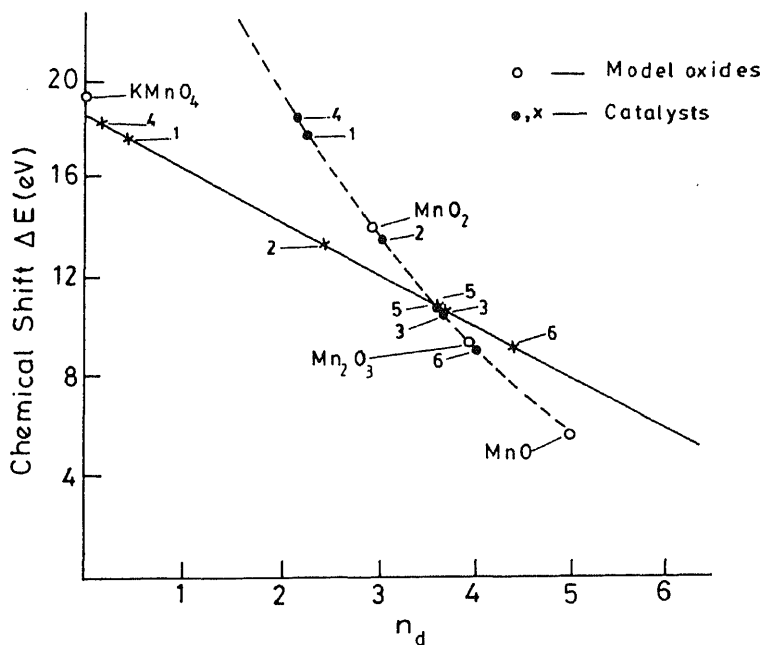


Figure 2. Plot of the chemical shift against the number of *d* electrons, n_d . 1. MnO₂ activated; 2. MnO₂ deactivated; 3. MnO₂ reduced; 4. MnO₂-SiO₂ activated; 5. MnO₂-SiO₂ deactivated; 6. MnO₂-SiO₂ reduced.

ΔE and the number of *d* electrons of MnO, Mn₂O₃ and MnO₂ is essentially parabolic. The point due to KMnO₄ deviates markedly from this parabolic plot possibly due to the different coordination and bonding in KMnO₄. We can draw a mean line taking all the points (MnO, Mn₂O₃, MnO₂ and KMnO₄) into account. We have estimated the number of *d*-electrons, n_d in the catalyst samples from both the working plots in figure 2. The range of n_d in the catalysts obtained from the two plots are given in table 1. The values of n_d in deactivated and reduced MnO₂ and MnO₂-SiO₂ catalysts are around the same from the two plots, but differ considerably in the case of the activated catalysts. The n_d values of the activated samples turn out to be 2.5 for MnO₂ and 2.4 for MnO₂-SiO₂ from the parabolic working plot based on MnO, Mn₂O₃ and MnO₂; from the working curve which includes KMnO₄, n_d is too low (0.5 and 0.2 for activated MnO₂ and MnO₂-SiO₂ catalysts respectively). The correct value is likely to be in between these two extremes. It appears that x-ray absorption edge measurements cannot provide good estimates of the number of *d*-electron states (or the oxidation state of the metal in these catalysts). This limitation may be because the chemical shift is really related to the effective atomic charge of the metal rather than the oxidation state or the number of *d*-electrons (Sankar *et al* 1983).

A feature of the x-ray absorption spectra which is sensitive to the number of *d*-electrons of the metal is the intensity of $1s \rightarrow 3d$ transition. The $1s \rightarrow 3d$ peak intensity can be normalised with respect to the intensity of the $1s \rightarrow 4p$ transition, which does not vary (Knapp *et al* 1982) since the $4p$ occupancy remains the same through the series of

Table 1. K-absorption edge and Auger results on MnO₂ catalysts and model compounds.

	K-absorption edge			Auger	
	$\Delta E(\text{eV})^a$	n_d^b	$I(1s \rightarrow 3d)/I(1s \rightarrow 4p)$	$I(\text{LVV})/I(\text{LMV})$	n_d
Mn	—	—	—	0.347 ^c	5
MnO	5.4	5	—	0.297	5
Mn ₂ O ₃	9.0	4	—	0.251	4
MnO ₂	13.9	3	—	0.220	3
KMnO ₄	19.1	0	—	—	—
1. MnO ₂	17.3	0.5–2.5	0.11	0.185	1.6
2. MnO ₂ deactivated	13.4	2.6–3.1	0.10	0.230	3.2
3. MnO ₂ reduced	10.4	3.7–3.8	0.09	0.237	3.4
4. MnO ₂ -SiO ₂ activated	18.1	0.2–2.4	0.24	0.162	1.0
5. MnO ₂ -SiO ₂ deactivated	10.6	3.6–3.7	0.11	0.240	3.5
6. MnO ₂ -SiO ₂ reduced	8.9	4.0–4.4	0.07	0.245	3.7

^a With reference to Mn metal; ^b range in the number of *d*-electrons given by the two plots in figure 2; ^c in Mn metal, we have to take the two 4*s* electrons into account since it is the total number of valence electrons that determines the metal Auger intensity ratio.

catalysts are listed in table 1 to illustrate the progressive increase in the intensity ratio as we go from the reduced form to the activated form of MnO₂; the deactivated form shows an intermediate value. This reflects that the *d* orbital occupancy of the metal in activated MnO₂ is lower than that in deactivated MnO₂ which in turn is lower than that in reduced MnO₂. We find similar behaviour in MnO₂-SiO₂ catalysts where the activated MnO₂-SiO₂ sample shows the highest intensity ratio corresponding to the lowest occupancy of the *d*-orbital.

3.2 Auger studies

X-ray induced Mn(LVV) and Mn(LMV) Auger spectra of manganese metal, MnO₂ and activated MnO₂ are shown in figure 3. Unlike the LMV transition, the LVV transition shows significant changes in intensity as well as width. This is expected since the two-hole final state in the LVV transition would be more sensitive to changes in the number of valence electrons ($3d + 4s$) as compared to the one-hole final state in the LMV transition.

In order to determine the number of *d* electron states in MnO₂ catalysts, we have made use of the LVV/LMV intensity ratios. These ratios in the Mn metal, reference oxides and catalyst samples are listed in table 1. A plot of the ratios in Mn metal and the reference oxides against the total number of valence electrons, *n*, is essentially linear (figure 4); the number of *d* electron states, *n_d* is given by *n*-2. In figure 4, we have also shown the LVV/LMV ratios corresponding to the variously treated MnO₂ and MnO₂-SiO₂ catalysts. We readily see that the value of *n_d* is significantly lower (oxidation state of Mn is higher) in activated MnO₂ and MnO₂-SiO₂ compared to ordinary MnO₂ prepared by the decomposition of the nitrate. The reduced catalysts, on the other hand, have oxidation states between 4 and 4.5, which are indicated by the intensity ratio of the

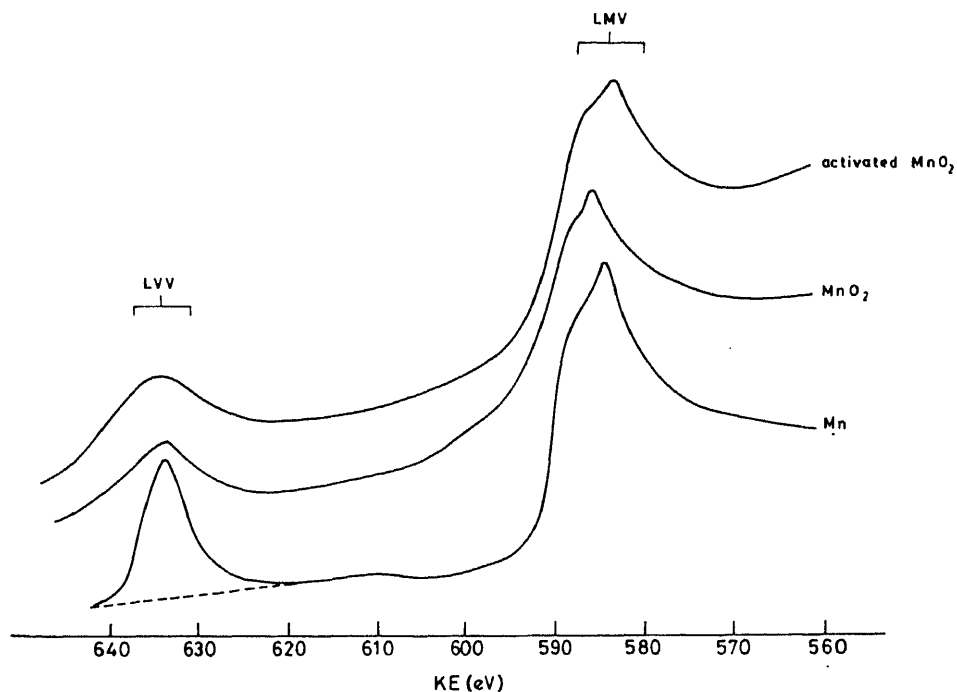


Figure 3. X-ray induced Auger transitions in the LVV and LMV regions of Mn.

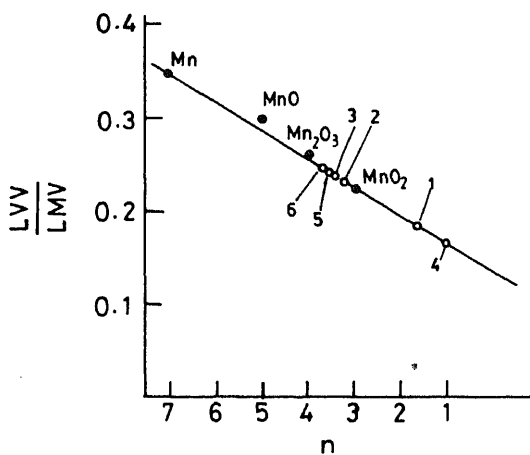


Figure 4. Plot of LVV/LMV Auger intensity ratio against the number of valence electrons, n ; the numbers designating points stand for the samples described in figure 2.

it should be pointed out that electron energy loss spectroscopy may also provide useful information on the number of *d* electron states of catalysts, but the study has hitherto been limited to model oxides only (Rao *et al* 1984a, b).

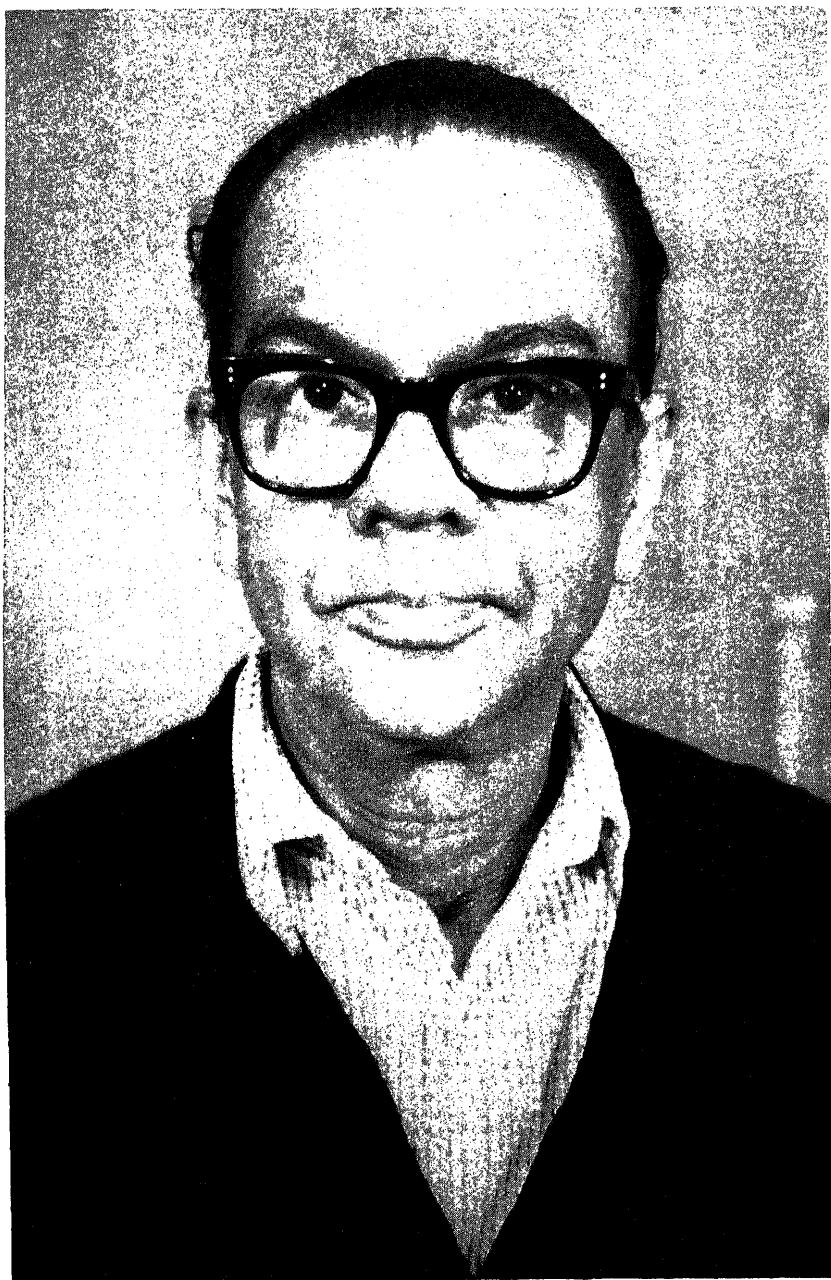
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**Dedicated to
Prof. Sadhan Basu, F.A.Sc.,
on the occasion of his sixtyfifth birthday**



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A generalization of Brillouin's theorem and the stability conditions in the quantum-mechanical variation principle in the case of general trial wave functions

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Abstract. In connection with the quantum-mechanical variation principle, it is shown that the Brillouin theorem and the stability conditions usually associated with the Hartree-Fock scheme in the many-electron theory may be generalized to the case of arbitrary trial functions depending on a set of linear or non-linear complex parameters.

1. The eigenvalue problem and the variation principle

The purpose of this paper is to show that the Brillouin theorem (Brillouin 1933, 1934) and the stability conditions (Thouless 1961; Adams 1962) usually associated with the Hartree-Fock scheme in many-electron theory are general features of the variation principle even in the case when the trial wave function is of a more general nature and depends on a set of linear or non-linear complex parameters.

Many of the fundamental problems in quantum mechanics may be formulated as eigenvalue problems with proper boundary conditions of the type

$$H\Psi = E\Psi, \quad (1)$$

or more generally

$$\Omega_1\Psi = \lambda\Omega_2\Psi, \quad (2)$$

where H , Ω_1 , and Ω_2 are self-adjoint operators; here we will also assume that Ω_2 is positive definite. If one introduces the variational expression

$$I = \langle \Phi | \Omega_1 | \Phi \rangle / \langle \Phi | \Omega_2 | \Phi \rangle = A/B, \quad (3)$$

where Φ is an arbitrary trial wave function, the eigenvalue problem (2) is equivalent with the variation principle:

$$\delta I = 0, \quad (4)$$

for the first-order variation. In a previous paper (Löwdin *et al* 1981), we considered the

change of I associated with a finite variation

$$\Delta\Phi = \Phi' - \Phi \quad (5)$$

of the trial wave function Φ ; one has

$$\begin{aligned} \Delta I = I' - I &= (A'/B') - (A/B) = (1/B') (A' - IB') = \\ &= (1/B') (\Delta A - I\Delta B). \end{aligned} \quad (6)$$

Introducing the combined operator

$$Q = \Omega_1 - I\Omega_2, \quad (7)$$

we obtained:

$$\begin{aligned} B'I = \Delta A - I\Delta B &= \langle \Delta\Phi | Q | \Phi \rangle + \langle \Phi | Q | \Delta\Phi \rangle + \\ &+ \langle \Delta\Phi | Q | \Delta\Phi \rangle, \end{aligned} \quad (8)$$

where the quantity $B' = \langle \Phi' | \Omega_2 | \Phi' \rangle$ is always positive.

In the treatment of a many-particle system, let us now introduce a general trial wave function Φ which depends not only on the particle coordinates but also on a set of linear or non-linear complex parameters

$$\begin{aligned} \mathbf{c} &= \{c_1, c_2 \dots c_p\}; \\ \Phi &= \Phi(\mathbf{c}) = \Phi(c_1, c_2, \dots c_p). \end{aligned} \quad (9)$$

Giving these parameters a finite variation, so that $c'_k = c_k + \Delta c_k$, one obtains the Taylor expansion

$$\Delta\Phi = \Phi(\mathbf{c} + \Delta\mathbf{c}) - \Phi(\mathbf{c}) = \sum_k \Delta c_k \cdot \Phi_k + \frac{1}{2!} \sum_{k,l} \Delta c_k \Delta c_l \Phi_{kl} + \dots, \quad (10)$$

where

$$\Phi_k = \frac{\partial \Phi}{\partial c_k}, \quad \Phi_{kl} = \frac{\partial^2 \Phi}{\partial c_k \partial c_l} = \Phi_{lk}, \dots \quad (11)$$

Substitution of this expression into (8) gives directly

$$\begin{aligned} B' \Delta I &= 2\text{Re} \sum_k \Delta c_k^* \langle \Phi_k | Q | \Phi \rangle + \\ &+ \text{Re} \sum_{k,l} \Delta c_k^* \Delta c_l^* \langle \Phi_{kl} | Q | \Phi \rangle + \sum_{k,l} \Delta c_k^* \langle \Phi_k | Q | \Phi_l \rangle \Delta c_l \\ &+ \text{terms of higher order.} \end{aligned} \quad (12)$$

At this point, we will assume that the variations Δc_k are small and that we will consider the quantity $B' \Delta I$ up to the second order. Separating the variations into their real and imaginary parts:

$$\Delta c_k = \Delta c_{k,r} + i \Delta c_{k,i} \quad (13)$$

$$\begin{aligned}
B' \cdot \Delta I &= \sum_k \{ (\Delta a_k - i \Delta b_k) \langle \Phi_k | Q | \Phi \rangle + (\Delta a_k + i \Delta b_k) \langle \Phi | Q | \Phi_k \rangle \} \\
&= \sum_k \Delta a_k \{ \langle \Phi_k | Q | \Phi \rangle + \langle \Phi | Q | \Phi_k \rangle \} - \\
&\quad - i \sum_k \Delta b_k \{ \langle \Phi_k | Q | \Phi \rangle - \langle \Phi | Q | \Phi_k \rangle \} = 0,
\end{aligned} \tag{14}$$

for all possible real Δa_k and Δb_k . Hence, the extreme values of I are determined by the conditions

$$\langle \Phi_k | Q | \Phi \rangle = 0, \tag{15}$$

for $k = 1, 2, \dots, p$, which is a generalization of the well-known Brillouin theorem. Here $\Phi_k = \partial \Phi / \partial c_k$ are the first derivatives of Φ at those values of the parameters $\mathbf{c} = \{c_1, c_2, \dots, c_p\}$ which characterize a particular extreme value. In the Hartree-Fock and projected Hartree-Fock schemes (Löwdin *et al* 1981), one starts from a single Slater determinant D built up from N one-electron wave functions ψ_k , which are then varied according to the formula

$$\psi'_k = \psi_k + \Delta c_k \bar{\psi}_k, \tag{16}$$

where $\bar{\psi}_k$ is assumed to be orthogonal to all the functions ψ_k for $k = 1, 2, \dots, N$. It is evident that the relations (15) give the condition for the 'best' trial wave function obtainable from the variation principle.

As a simple example of the linear case, let us introduce a many-particle basis $\phi = \{\phi_k\}$ and let us expand the trial function Φ in the form:

$$\Phi = \sum_k \phi_k c_k. \tag{17}$$

One gets immediately $\Phi_k = \phi_k$ and $\Phi_{kl} = 0$, and the condition (15) gives then

$$\langle \phi_k | Q | \Phi \rangle = \sum_l \langle \phi_k | Q | \phi_l \rangle c_l = 0, \tag{18}$$

which is the standard linear equation system for the coefficients c_l with the approximate eigenvalues I determined by the secular equation:

$$|\langle \phi_k | \Omega_1 - I \Omega_2 | \phi_l \rangle| = 0. \tag{19}$$

The generalized Brillouin theorem (15), hence, gives a connection between the linear 'configurational interaction' method and the non-linear Hartree-Fock scheme.

2. Stability condition and instabilities

In order to treat the second-order variations in the right-hand side of expression (12), it is convenient to introduce the matrices $\mathbf{A} = \{A_{kl}\}$ and $\mathbf{B} = \{B_{kl}\}$ having elements defined through the relations:

$$A_{kl} = \langle \Phi_k | Q | \Phi_l \rangle, B_{kl} = \langle \Phi_{kl} | Q | \Phi \rangle, \tag{20}$$

and to separate them into their real and imaginary parts:

$$\mathbf{A} = \mathbf{A}_1 + i\mathbf{A}_2, \quad \mathbf{B} = \mathbf{B}_1 + i\mathbf{B}_2. \quad (21)$$

Since Q is a self-adjoint operator, one has $\mathbf{A}^\dagger = \mathbf{A}$, which implies:

$$\tilde{\mathbf{A}}_1 = \mathbf{A}_1, \quad \tilde{\mathbf{A}}_2 = -\mathbf{A}_2, \quad (22)$$

where the symbol $\sim$ indicates the transposed matrix with rows and columns interchanged. Since $\mathbf{B}_{kl} = \mathbf{B}_{lk}$, the matrix $\mathbf{B}$ is a symmetric matrix with complex elements, and the relation $\tilde{\mathbf{B}} = \mathbf{B}$ gives:

$$\tilde{\mathbf{B}}_1 = \mathbf{B}_1, \quad \tilde{\mathbf{B}}_2 = \mathbf{B}_2. \quad (23)$$

For the last term in the right-hand side of (12), one obtains now—observing that the imaginary part vanishes identically:

$$\begin{aligned} t_1 &= \sum_{k,l} \Delta c_k^* \langle \Phi_k | Q | \Phi_l \rangle \Delta c_l = \Delta \mathbf{c}^\dagger \mathbf{A} \Delta \mathbf{c} \\ &= (\Delta \tilde{\mathbf{a}} - i\Delta \tilde{\mathbf{b}}) (\mathbf{A}_1 + i\mathbf{A}_2) (\Delta \mathbf{a} + i\Delta \mathbf{b}) \\ &= \Delta \tilde{\mathbf{a}} \cdot \mathbf{A}_1 \cdot \Delta \mathbf{a} - \Delta \tilde{\mathbf{a}} \cdot \mathbf{A}_2 \cdot \Delta \mathbf{b} + \Delta \tilde{\mathbf{b}} \cdot \mathbf{A}_2 \cdot \Delta \mathbf{a} + \Delta \tilde{\mathbf{b}} \cdot \mathbf{A}_1 \cdot \Delta \mathbf{b} \\ &= (\Delta \tilde{\mathbf{a}}, \Delta \tilde{\mathbf{b}}) \begin{pmatrix} \mathbf{A}_1 & -\mathbf{A}_2 \\ \mathbf{A}_2 & \mathbf{A}_1 \end{pmatrix} \begin{pmatrix} \Delta \mathbf{a} \\ \Delta \mathbf{b} \end{pmatrix}. \end{aligned} \quad (24)$$

For the other second-order term in the right-hand side of (12), one obtains similarly:

$$\begin{aligned} t_2 &= \text{Re} \sum_{k,l} \Delta c_k^* \langle \Phi_{kl} | Q | \Phi \rangle \Delta c_l^* = \text{Re} \Delta \mathbf{c}^\dagger \mathbf{B} \Delta \mathbf{c}^* \\ &= \text{Re} (\Delta \tilde{\mathbf{a}} - i\Delta \tilde{\mathbf{b}}) (\mathbf{B}_1 + i\mathbf{B}_2) (\Delta \mathbf{a} - i\Delta \mathbf{b}) \\ &= \Delta \tilde{\mathbf{a}} \cdot \mathbf{B}_1 \cdot \Delta \mathbf{a} + \Delta \tilde{\mathbf{a}} \cdot \mathbf{B}_2 \cdot \Delta \mathbf{b} + \Delta \tilde{\mathbf{b}} \cdot \mathbf{B}_2 \cdot \Delta \mathbf{a} - \Delta \tilde{\mathbf{b}} \cdot \mathbf{B}_1 \cdot \Delta \mathbf{b} \\ &= (\Delta \tilde{\mathbf{a}}, \Delta \tilde{\mathbf{b}}) \begin{pmatrix} \mathbf{B}_1 & \mathbf{B}_2 \\ \mathbf{B}_2 & -\mathbf{B}_1 \end{pmatrix} \begin{pmatrix} \Delta \mathbf{a} \\ \Delta \mathbf{b} \end{pmatrix}. \end{aligned} \quad (25)$$

Introducing the column vector

$$\mathbf{d} = \begin{pmatrix} \Delta \mathbf{a} \\ \Delta \mathbf{b} \end{pmatrix} \quad (26)$$

of order $2p$ and the real symmetric matrix

$$\bar{\mathbf{T}} = \begin{pmatrix} \mathbf{A}_1 + \mathbf{B}_1, & -\mathbf{A}_2 + \mathbf{B}_2 \\ \mathbf{A}_2 + \mathbf{B}_2, & \mathbf{A}_1 - \mathbf{B}_1 \end{pmatrix} \quad (27)$$

of order $2p \times 2p$, one gets finally the following result for the second-order part ($t_1 + t_2$):

$$\mathbf{B}' \cdot \mathbf{I} = \tilde{\mathbf{d}} \bar{\mathbf{T}} \mathbf{d}. \quad (28)$$

The result is structurally the same as in the previous paper (Löwdin *et al* 1981), except that the matrices $\mathbf{A}$ and $\mathbf{B}$ now have different interpretations; we note particularly that $\mathbf{B}$ may have non-vanishing diagonal elements.

The extreme value I corresponding to the conditions (15) is hence a *true minimum*, if

the matrix $\bar{T}$ is positive definite, i.e. if all the eigenvalues of $\bar{T}$ are positive. To prove that this is the case is often both difficult and time-consuming, and most of the work so far has instead been devoted to studying instabilities, i.e. extreme values of a different character.

If there are any variations d , for which the right-hand side of (28) becomes *negative*, one is dealing with an unstable extreme value or 'instability.' This will, of course, always occur if the matrix $\bar{T}$ has one or more negative eigenvalues. For real variations Δc , it will also occur if the matrix $A_1 + B_1$ has any negative eigenvalues, and, for pure imaginary variations Δc , it will occur if the matrix $A_1 - B_1$ has any negative eigenvalues, etc. In fact, the number of possibilities turns out to be very large. It remains to be investigated to what extent these instabilities in the case of a general trial function may be classified in the same way as in the Hartree-Fock scheme (Cizek and Paldus 1967, 1970; Fukutome 1968, 1971, 1972, 1973a, b, 1974, 1975; Paldus and Cizek 1969, 1970a, b, 1971; Paldus 1970; Paldus *et al* 1973, 1978; Laforgue *et al* 1973; Laidlaw 1973; Paldus and Veillard 1977, 1978; Ozaki and Fukutome 1978; Ozaki 1979, 1980; Benard and Paldus 1980; Fukutome 1981). It is also illustrative to discuss the standard 'configurational interaction' method as described by (17-19) from this point of view.

3. Search for the extreme values

It is evident that, if the conditions (15) for an extreme value are not satisfied for a specific set of parameter values $c = \{c_1, c_2, \dots, c_p\}$:

$$f_k = \langle \Phi_k | Q | \Phi \rangle \neq 0, \quad (29)$$

one may use the technique developed here to search for a better approximation $c' = c + \Delta c$ to an extreme value. One gets directly:

$$\begin{aligned} f'_k &= \langle \Phi'_k | Q | \Phi' \rangle = \langle \Phi_k + \Delta \Phi_k | Q | \Phi + \Delta \Phi \rangle \\ &= \langle \Phi_k | Q | \Phi \rangle + \sum_l \Delta c_l^* \langle \Phi_{kl} | Q | \Phi \rangle + \sum_l \langle \Phi_k | Q | \Phi_l \rangle \Delta c_l + \dots \\ &= f_k + \sum_l B_{kl} \Delta c_l^* + \sum_l A_{kl} \Delta c_l + \dots = 0, \end{aligned} \quad (30)$$

or

$$f' = f + A \Delta c + B \Delta c^* + \dots = 0. \quad (31)$$

Separating the real and imaginary parts of each term, one obtains with $f = f_1 + i f_2$:

$$\begin{cases} f_1 + (A_1 + B_1; -A_2 + B_2) \begin{pmatrix} \Delta a \\ \Delta b \end{pmatrix} = 0; \\ f_2 + (A_2 + B_2; A_1 - B_1) \begin{pmatrix} \Delta a \\ \Delta b \end{pmatrix} = 0; \end{cases} \quad (32)$$

i.e.

$$\begin{pmatrix} \Delta a \\ \Delta b \end{pmatrix} = -(\bar{T})^{-1} \begin{pmatrix} f_1 \\ f_2 \end{pmatrix}. \quad (33)$$

This means that the matrix $\bar{T}$ and its inverse may be of essential importance also in the search for the extreme values.

In practice, one does not evaluate the inverse of the matrix $\bar{\mathbf{T}}$ but solves the equation system

$$\bar{\mathbf{T}} \begin{pmatrix} \Delta \mathbf{a} \\ \Delta \mathbf{b} \end{pmatrix} = - \begin{pmatrix} \mathbf{f}_1 \\ \mathbf{f}_2 \end{pmatrix}, \quad (34)$$

by some of the standard methods available. This leads to a better approximation for the vector $\mathbf{c}$, and one may then repeat the procedure, until the condition $\mathbf{f} = \mathbf{0}$ becomes satisfied with the accuracy desired. Equation (33) gives the connection between some of the current algorithms for finding extreme values of I and the stability conditions.

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Translational and rotational symmetries in third integral derivatives

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Abstract. Based on the invariance under translations and rotations of quantum chemical one- and two-electron integrals, a method for obtaining a complete set of independent relations among third integral derivatives is presented. It is shown that the number of dependent integral derivatives, which is equal to the number of independent relations, can be straightforwardly determined in terms of the remaining third derivatives which must be explicitly calculated. The set of such independent and dependent third integral derivatives can be chosen in a manner which imposes no restrictions on the nuclear positions. The special case of collinear nuclear centres is also separately analyzed.

Keywords. Translational symmetry; rotational symmetry.

1. Introduction

The direct computation of analytical derivatives of the electronic energy with respect to nuclear coordinates has proved to be a powerful tool because it yields an immediate sense of the local topography of the energy surface. Recently, workers (Pulay 1983; Simons and Jørgensen 1984; Simons *et al* 1984) have extended techniques for calculating first and second derivatives to the calculation of anharmonicities of the energy surface.

A large number of third integral derivatives need to be calculated in order to implement a calculation of the third derivative of the energy surface. For example, consider the third derivatives of four-centre two-electron integrals in a calculation involving n primitive atomic basis functions. One can easily show that there are 364 third integral derivatives for each of the n^4 such integrals. In the N -centre case there are $(3N)(3N+1)(3N+2)/6$ third derivatives for each of the n^4 integrals.

Use of translational and rotational invariance (or symmetry) has proved to be a valuable tool in calculating derivatives of the energy surface by reducing the number of integral derivatives that need to be explicitly calculated (Komornicki *et al* 1977; Dupuis and King 1978; Kahn 1981; Takada *et al* 1981; Vincent and Schaefer 1983; Vincent *et al* 1983; Page *et al* 1984; Schlegel *et al* 1984; Banerjee *et al* 1985). The goal of this paper is to extend the formalism of an earlier paper (Banerjee *et al* 1985) to third integral derivatives. The present work provides a complete analysis of the invariance properties for third integral derivatives. We provide a method for treating the redundancy of invariance conditions. Such a treatment is absent from earlier work. Rotational

invariance conditions are geometry dependent in the sense that poorly chosen conditions impose many geometrical constraints on the molecule. We present a systematic method for choosing the conditions in a manner which imposes no restrictions on the allowable geometries of the nuclear positions. In §2 we use translation and rotation operators to derive the essential invariance relations involving third integral derivatives. In §3 we derive a method for finding the independent integral derivatives and for explicitly calculating the remaining (dependent) integral derivatives using symmetry relations.

2. Theoretical development

An integral I depends upon the gaussian basis functions appearing in I . Each of the gaussians is centred at one of the nuclear positions $\mathbf{P}_K$ ($K = 1, N; N \leq 4$)

$$I = I\{G_1(\mathbf{P}_1, \mathbf{r}_1), G_2(\mathbf{P}_2, \mathbf{r}_2) \dots G_N(\mathbf{P}_N, \mathbf{r}_N)\}. \quad (1)$$

Each cartesian gaussian function is parameterized in terms of the centre $\mathbf{P}_K$ and the internal coordinate $\mathbf{r}_K$ as

$$G_K(\mathbf{P}_K, \mathbf{r}_K) = A(X - P_{Kx})^{n_x} (Y - P_{Ky})^{n_y} (Z - P_{Kz})^{n_z} \exp(-\xi r_K^2), \quad (2)$$

where A is the normalization constant and the vector $\mathbf{R}$ is the lab fixed coordinate with components X, Y, Z giving the location of the electron relative to the origin.

$$\mathbf{R} = \mathbf{P}_K + \mathbf{r}_K; \quad K = 1, N. \quad (3)$$

An operator $\hat{T}$ that involves a translation of all points in space by a vector $\mathbf{t} = (t_x, t_y, t_z)$ can be written as

$$\hat{T} = \exp\{-\mathbf{t} \cdot \nabla_{\mathbf{R}}\} \quad (4)$$

where $\nabla_{\mathbf{R}} = (\partial/\partial X, \partial/\partial Y, \partial/\partial Z)$ defines the gradient operator at all points $\mathbf{R}$ in space. An operator $\hat{R}$ that generates a rotation by the angle $\phi = (\phi_x, \phi_y, \phi_z)$ about an axis along the direction ϕ through the lab fixed origin can be expressed as

$$\hat{R}(\phi) = \exp\{-\phi \cdot \mathbf{L}\}, \quad (5)$$

where

$$\mathbf{L} = \mathbf{R} \times \nabla_{\mathbf{R}}. \quad (6)$$

For two-electron integrals, which depend on two electronic coordinates $\mathbf{R}$ and $\mathbf{R}'$, the $\nabla_{\mathbf{R}}$ operator will be implicitly assumed to operate on both variables (i.e., it is $\nabla_{\mathbf{R}} + \nabla_{\mathbf{R}'}$). Also from the form of the gaussian function it is seen that

$$\frac{\partial}{\partial X} G_K(\mathbf{P}_K, \mathbf{r}_K) = -\frac{\partial}{\partial P_{Kx}} G_K(\mathbf{P}_K, \mathbf{r}_K) = \frac{\partial}{\partial x_K} G_K(\mathbf{P}_K, \mathbf{r}_K). \quad (7)$$

gaussian is

$$\begin{aligned} L_z G_K(\mathbf{P}_K, \mathbf{r}_K) &= \left(X \frac{\partial}{\partial Y} - Y \frac{\partial}{\partial X} \right) G(\mathbf{P}_K, \mathbf{r}_K) \\ &= \left\{ - \left(P_{Kx} \frac{\partial}{\partial P_{Ky}} - P_{Ky} \frac{\partial}{\partial P_{Kx}} \right) + \left(x_K \frac{\partial}{\partial y_K} - y_K \frac{\partial}{\partial x_K} \right) \right\} G(\mathbf{P}_K, \mathbf{r}_K) \\ &\equiv \{ -L_{zK} + l_{zK} \} G_K(\mathbf{P}_K, \mathbf{r}_K). \end{aligned} \quad (8)$$

Thus L_z can be written as the sum of an operator L_{zK} which acts only on nuclear coordinates $\mathbf{P}_K$ and an operator l_{zK} which acts only on the internal coordinate $\mathbf{r}_K$.

Since an integral is unchanged when all of its coordinates are translated or rotated, we can write

$$I\{G_1, G_2, \dots\} = I\{\hat{T}(G_1, G_2, \dots)\} \quad (9)$$

and

$$I\{G_1, G_2, \dots\} = I\{\hat{R}(G_1, G_2, \dots)\}. \quad (10)$$

Equations (9) and (10) also hold when I is replaced by a first derivative $\partial I / \partial P_K$ or by a second derivative $\partial^2 I / \partial P_K \partial P_J$. The RHS of (9) is then expanded in a power series in $\mathbf{t}$. The terms of each order in $\mathbf{t}$ are separately set to zero yielding through third-order the relations

$$T^{(1)} I = \sum_{J\alpha} I_{J\alpha} = 0, \quad (11)$$

$$T^{(2)} I = \sum_{JK} I_{J\alpha K\beta} = 0,$$

$$T^{(3)} I = \sum_{JKL} I_{J\alpha K\beta L\gamma} = 0, \quad \alpha, \beta, \gamma = x, y, z,$$

where the shorthand notation

$$I_{J\alpha} = \frac{\partial I}{\partial P_{J\alpha}}, \quad I_{J\alpha K\beta} = \frac{\partial^2 I}{\partial P_{J\alpha} \partial P_{K\beta}}, \quad \text{etc.}$$

has been introduced.

There are three ways to generate relations involving third integral derivatives from the above conditions:

$$T^{(3)} I = \sum_{JKL} I_{J\alpha K\beta L\gamma} = 0, \quad (12)$$

$$\partial / \partial P_{L\gamma} (T^{(2)} I) = \sum_{JK} I_{J\alpha K\beta L\gamma} = 0, \quad (13)$$

$$\partial^2 / \partial P_{K\beta} \partial P_{J\alpha} (T^{(1)} I) = \sum_{L\gamma} I_{J\alpha K\beta L\gamma} = 0. \quad (14)$$

powers of ϕ . Again there are three ways to generate rotational conditions among the derivatives:

$$R^{(3)}I = \mathbf{L} \mathbf{L} \mathbf{L} I = 0,$$

$$\partial^2 / \partial P_{J\mu} \partial P_{K\nu} (R^{(1)}I) = \partial^2 / P_{J\mu} \partial P_{K\mu} (\mathbf{L}I) = 0$$

$$\partial / \partial P_{J\mu} (R^{(2)}I) = \partial / \partial P_{J\mu} (\mathbf{L} \mathbf{L} I) = 0$$

It can be shown that the relations in (17) can be used to generate all of the relations (15) and (16). Thus we need only look at Eq. (17).

Equation (8) is substituted into (17) to yield

$$\sum_{J=1}^N L_{\gamma J} I_{K\mu M\nu} = \sum_{J=1}^N l_{\gamma J} I_{K\mu M\nu} \quad K, M = 1, N; \quad \gamma, \mu, \nu = x, y, z.$$

The operator $L_{\gamma J}$ has been pulled outside of the integral $I_{K\mu M\nu}$ since the $\mathbf{P}_J$, which involves, are not integration variables. In addition, the notation $l_{\gamma J} I_{K\mu M\nu}$ has been introduced to denote that the $l_{\gamma J}$ operator is applied to the vector $\mathbf{r}$ in the gaussian appearing in $I_{K\mu M\nu}$. That is, $l_{\gamma J} I_{K\mu M\nu}$ represents $I_{K\mu M\nu} (l_{\gamma J} G_J)$.

Substituting the definitions of $L_{\gamma J}$ and $l_{\gamma J}$ into (18) we then obtain

$$\sum_{J=1}^N (P_{J\alpha} I_{J\beta K\mu M\nu} - P_{J\beta} I_{J\alpha K\mu M\nu}) = I_{\alpha\beta K\mu M\nu}, \quad (19)$$

$$\alpha\beta = xy, yz, zx; \quad K, M = 1, N; \quad \mu, \nu = x, y, z; \quad (K\mu) \geq (M\nu),$$

where

$$I_{\alpha\beta K\mu M\nu} = \sum_{J=1}^N l_{\gamma J} I_{K\mu M\nu} - \delta_{\alpha\mu} I_{K\beta M\nu} + \delta_{\beta\mu} I_{K\alpha M\nu} - \delta_{\alpha\nu} I_{K\mu M\beta} + \delta_{\beta\nu} I_{K\mu M\alpha} \\ \alpha\beta\gamma = xyz, yzx, zxy. \quad (20)$$

The $l_{\alpha J}$ operator transforms a gaussian into two gaussians in the same shell. Using as an example we see that

$$l_{zJ} G_J(n_x, n_y, n_z) = \left(x_J \frac{\partial}{\partial y_J} - y_J \frac{\partial}{\partial x_J} \right) G_J(n_x, n_y, n_z) \\ = n_y \left(\frac{2n_x + 1}{2n_y - 1} \right)^{1/2} G_J(n_x + 1, n_y - 1, n_z) \\ - n_x \left(\frac{2n_y + 1}{2n_x - 1} \right)^{1/2} G_J(n_x - 1, n_y + 1, n_z).$$

Thus we see that the RHS of (19a) is a linear combination of second derivative integrals.

3. Implementation

The relations in (14) and (19) are not independent. A systematic method must be developed to eliminate the redundant relations and to best utilize the remaining (independent) ones.

As a first step we rewrite (14) as

$$I_{NaK\beta L\gamma} = \sum_{J=1}^{N-1} I_{JaK\beta L\gamma}, \quad (21a)$$

$$\alpha, \beta, \gamma = x, y, z; K, L = 1, N-1; (K\beta) \geq (L\gamma),$$

$$I_{NaN\beta L\gamma} = \sum_{K=1}^{N-1} I_{NaK\beta L\gamma}, \quad (21b)$$

$$\alpha\beta = xy, yz, zx, xx, yy, zz; \gamma = x, y, z; L = 1, N-1,$$

$$I_{NaN\beta N\gamma} = \sum_{L=1}^{N-1} I_{NaN\beta L\gamma}, \quad (21c)$$

$$\alpha\beta\gamma = xxx, xxy, xxz, xyy, xyz, xzz, yyy, yyz, yzz, zzz,$$

where we have given the centres some arbitrary numbering from 1 to N . A straightforward calculation shows that (21) contain $\{3(3N-3)(3N-2)/2 + 18(N-1) + 10\}$ conditions which relate certain third integrals derivatives to others.

The next step is to substitute (21) into the rotational-invariance relations of (19). This allows all reference to atom N to be removed from the rotational conditions. The result is

$$\sum_{J=1}^{N-1} (\tilde{P}_{Ja} I_{J\beta K\mu M\nu} - \tilde{P}_{J\beta} I_{Ja K\mu M\nu}) = I_{a\beta K\mu M\nu} \quad (22)$$

$$\alpha\beta = xy, yz, zx; K, M = 1, N-1; \mu, \nu = x, y, z; (K\mu) \geq (M\nu),$$

where $\tilde{P}_{Ja} = P_{Ja} - P_{Na}$. There are $\{3(3N-3)(3N-2)/2\}$ conditions in (22). Equations (21) and (22) thus yield a total of $\{27N^2 - 27N + 10\}$ relations among third integral derivatives.

For an N -centre integral there are $\{(3N)(3N+1)(3N+2)/6\}$ third derivatives of the integral. We will show that the number of *independent* third derivatives is $\{N'(N'+1)(N'+2)/6\}$ where $N' = 3N-6$ ($3N-5$ for collinear geometries).

Non-collinear case:

The total number of *dependent* third integral derivatives that we expect is

$$\frac{1}{6} \{(3N)(3N+1)(3N+2) - (3N-6)(3N-5)(3N-4)\} = 27N^2 - 36N + 20.$$

Since there are $\{27N^2 - 27N + 10\}$ relations among the integral derivatives and only $\{27N^2 - 36N + 20\}$ dependent integral derivatives, there must be $\{9N - 10\}$ too many relations. These excess relations can be removed via what we called in an earlier paper (Banerjee *et al* 1985) relations among the relations (RAR). It is easily seen that the relations given in (21) are in fact independent. The dependent relations are therefore contained in (22).

We discovered a class of RAR of (22) for third derivatives given by

$$\sum_{J=1}^{N-1} \{\tilde{P}_{J\gamma} E_{a\beta J\beta K\mu} + \tilde{P}_{Ja} E_{\beta\gamma J\beta K\mu} - \tilde{P}_{J\beta} (E_{a\beta J\gamma K\mu} + E_{\beta\gamma Ja K\mu})\} = 0, \quad (23)$$

values of α, β, K, μ, M , and v . These $\{9N - 9\}$ RAR can be verified by simple substitution. In fact, only $\{9N - 10\}$ of the above RAR are independent.

Since atom 1 and atom N are on different centres, $\tilde{P}_{1x}, \tilde{P}_{1y}$, or $\tilde{P}_{1z}$ has to be nonzero. For ease of notation we will assume that $\tilde{P}_{1y} \neq 0$. The cases where $\tilde{P}_{1y} = 0$ but P_{1z} or P_{1x} is nonzero can be recovered by cyclic permutation of x, y , and z .

If $\tilde{P}_{1y} \neq 0$ then the $\{9N - 10\}$ relations that need to be discarded from (22) are of the form $\{E_{xyzK\mu}, E_{zx1xK\mu}, E_{zx1xK\mu} (K = 1, N - 1; \mu = x, y, z)\}$. The relation $E_{zx1xK\mu}$ appears twice in this list, and therefore there are $\{9N - 10\}$ unique relations. This list of relations can be obtained by writing (23) in matrix form and then using row operations to transform the matrix into a lower-echelon form using care to use *only* $\tilde{P}_{1y}$ as pivot elements.

Equation (22) then transforms into

$$\sum_{j=1}^{N-1} (\tilde{P}_{ja} I_{j\beta K\mu Mv} - \tilde{P}_{j\beta} I_{ja K\mu Mv}) = I_{a\beta K\mu Mv},$$

$$K, M = 1, N - 1; \alpha\beta = xy, yz, zx; \mu, v = x, y, z; (K\mu) \geq (Mv);$$

$$(E_{xyzMv}, E_{zx1zMv}, E_{zx1xMv}).$$

The discarded conditions $E_{xyzMv}, E_{zx1zMv}, E_{zx1xMv}$ are enclosed in parentheses above. Equation (24) can be thought of as a system of linear equations with $\{(27N^2 - 18N + 38)/2\}$ independent equations in $\{(9N^3 - 18N^2 + 11N - 2)/2\}$ variables (third derivatives).

We divide the variables into two groups, the dependent variables equal to the number of relations above and the independent variables that must be known from some other source. It is *not* possible to arbitrarily choose the dependent and independent variables in (24). Since the $\tilde{P}_{ja}$ are arbitrary (possibly zero), a bad choice of dependent variables will result in (24) being insoluble.

A non-collinear integral contains at least three centres. If $\tilde{P}_{1y} \neq 0$ then there exists a centre K such that either $(\tilde{P}_{Kx}\tilde{P}_{1y} - \tilde{P}_{Ky}\tilde{P}_{1x}) \neq 0$ or $(\tilde{P}_{Kz}\tilde{P}_{1y} - \tilde{P}_{Ky}\tilde{P}_{1z}) \neq 0$. If a centre K does not exist such that one of these is nonzero then the centres are collinear contrary to assumption. For the sake of simplicity we rename centre K as centre 2; this is simply a convention and has no consequences.

Let us assume for example that $(\tilde{P}_{2x}\tilde{P}_{1y} - \tilde{P}_{2y}\tilde{P}_{1x}) \neq 0$. Equation (24) can then be written as a matrix equation with the third derivatives as variables. For the three- and four-centre cases we have algebraically (Hearn 1984) reduced this matrix equation to echelon form using *only* $\tilde{P}_{1y}$ as pivot elements. For three-centre integrals the independent third derivatives are *all* the unique third derivatives constructed from the differential elements $\partial P_{1y}, \partial P_{2y}$, and ∂P_{2x} , which are to be explicitly calculated. Similarly, the 56 independent derivatives for the four-centre case can be constructed uniquely from the differential elements $\partial P_{1y}, \partial P_{2y}, \partial P_{2x}, \partial P_{3x}, \partial P_{3y}$, and ∂P_{3z} . For the above choice of the independent and dependent third derivatives the additional assumption $(\tilde{P}_{2x}\tilde{P}_{1y} - \tilde{P}_{2y}\tilde{P}_{1x}) \neq 0$ is required since (in addition to $\tilde{P}_{1y}$) they appear as the corresponding coefficients of the dependent derivatives in the echelon form.

derivatives $I_1, \dots, I_r$ are calculated straightforwardly from (24) as a solution of the simultaneous linear equation

$$\mathbf{A}_{(r \times r)} \begin{bmatrix} I_1 \\ \vdots \\ I_r \end{bmatrix} = -\mathbf{B}_{r \times (n-r)} \begin{bmatrix} I_{r+1} \\ \vdots \\ I_n \end{bmatrix} + \begin{bmatrix} b_1 \\ \vdots \\ b_r \end{bmatrix} \quad (25)$$

where $\mathbf{A}$ contains the r columns of the coefficient matrix of (24) corresponding to be the dependent derivatives $I_1 \dots I_r$, while $\mathbf{B}$ contains the corresponding columns for the $n-r$ independent integrals. The elements of the $\mathbf{b}$ vectors correspond to the right-hand side of (24).

Collinear case:

The total number of dependent third integral derivatives in this case is

$$\frac{1}{6} \{ (3N)(3N+1)(3N+2) - (3N-5)(3N-4)(3N-3) \} \\ = (45N^2 - 45N + 20)/2$$

Thus we have $\{(9N^2 - 9N)/2\}$ excess relations that need to be removed via RAR.

There exists another class of RAR given by the formula

$$\tilde{P}_{1z} E_{xyJ\mu K\nu} + \tilde{P}_{1x} E_{yzJ\mu K\nu} + \tilde{P}_{1y} E_{zxJ\mu K\nu} = 0 \quad (26)$$

$J, K = 1, N-1; \mu, \nu = x, y, z; (J\mu) \geq (K\nu).$

Equation (26) holds only in the collinear case. There are $\{(9N^2 - 15N + 6)/2\}$ RAR in (26). With (23) there are a total of $\{(9N^2 + 3N - 12)/2\}$ RAR. Again there is an excess of RAR. A detailed analysis shows that as expected there are only $\{9N^2 - 9N\}/2\}$ independent RAR in (23) and (26); one particular choice is to discard all of the relations of the form $\{E_{zxJ\mu K\nu}$ and $E_{xy1zJ\mu} (J, K = 1, N-1; \mu, \nu = x, y, z)\}$.

The analysis to find the dependent and independent variables is similar to that in the non-collinear case although no assumptions other than $\tilde{P}_{1y} \neq 0$ have to be made. If the above conditions are discarded, the independent variables are all the unique third derivatives that can be constructed from the differential element $\partial P_{1y}, \partial P_{2x}, \partial P_{2y}$, and ∂P_{2z} for the three-centre case and $\partial P_{1y}, \partial P_{2x}, \partial P_{2y}, \partial P_{2z}, \partial P_{3x}, \partial P_{3y}$, and ∂P_{3z} for the four-centre case. For the two-centre case the only third derivative that need be calculated is I_{1y1y1y} .

4. Discussion and conclusions.

Making a minimum number of choices of the geometry, we have shown how to choose a set of independent third integral derivatives, which needs to be explicitly calculated, and a set of dependent third integral derivatives that can be expressed in terms of the independent ones. Knowing the values of the independent third derivative integrals, it is possible to solve for the dependent integral derivatives by using (24) or (23) followed by (21).

the second derivatives obtained by Banerjee *et al* (1985). Analogous to (22) we have for the second derivatives

$$\sum_{j=1}^{N-1} (\tilde{P}_{j\alpha} I_{j\beta K\mu} - \tilde{P}_{j\beta} I_{j\alpha K\mu}) = I_{\alpha\beta K\mu} \quad (27)$$

$$\alpha\beta = xy, yz, zx; K = 1, N-1; \mu = x, y, z.$$

From (22) we discard relations of the form $\{E_{xy1zK\mu}, E_{zx1zK\mu}, E_{zx1xK\mu} (K = 1, N-1; \mu = x, y, z)\}$. For the second derivative case we discard the relations $\{E_{xy1z}, E_{zx1x}, E_{zx1y}\}$. For the three-centre case the independent variables are those third derivatives that can be constructed from the differentials $\partial P_{1y}, \partial P_{2y}, \partial P_{2z}$. In the second derivative case the dependent variables are those second derivatives that can be constructed from the differentials $\partial P_{1y}, \partial P_{2y}, \partial P_{2z}$. We feel that the results for fourth derivatives can be possibly written by inspection.

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Applications of a novel algorithm for the calculation of MCSCF wavefunction: a look into possible avenues of convergence acceleration

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Abstract. The efficacy of a method based on the direct inversion in the iterative subspace (DIIS) in accelerating the approach to self consistency in the calculation of the MCSCF wavefunction using a novel algorithm developed earlier, is compared with that of a simple damping technique. Although the 'damping' turns out to be ineffective in the 'quadratic region', it accelerates remarkably in the rate of descent on the energy hypersurface in the early stages of the iterative process which leads to an impressive overall increase in the rate of approach to self consistency. The DIIS based procedure turns out to be ineffective when coupled to the present method and is plagued by ill conditioning problems. Calculations are done to compute the equilibrium geometrical parameters, charge density on different atoms, and dipole moment of HNO molecule in the lowest $1,3\pi\pi^*$ states at the INDO/2-MCSCF level.

Keywords. Convergence acceleration; MC-SCF theory; through damping; direct inversion in the iterative subspace; orthogonal gradient method; orthonormality constrained variation method.

1. Introduction

The single determinant SCF theory and the simple orbital picture emerging from it has undoubtedly been extremely useful in interpreting and correlating a vast body of chemical facts. This simplicity and usefulness of the independent particle model notwithstanding, there are situations when one has to abandon this simple model and look for a more appropriate one. For example, the single configuration closed shell wavefunction fails to describe correctly the dissociation of a molecule into open shell fragments. In fact, whenever one or more configurations are energetically degenerate or quasi-degenerate with the main one, the single determinant representation for the wavefunction of the system breaks down. In such a situation we are forced to adopt a many configuration description of the wavefunction where each configuration represents a Slater determinant constructed from a set of orthonormal one-electron functions (orbitals). If we now set out to make energy stationary with respect to variations in the configuration weight factors as well as in the orbital forms, we arrive at what is known as the MCSCF method in quantum chemistry parlance. The pioneering

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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use of this method in atomic physics can be traced to the early work of Hartree and Seirles (1939). A generalized reformulation was later made by McWeeny (1955, 1956, 1960). Successful molecular calculations were made much later (Das and Wahl 1967; Clementi and Veillard 1967) and since then a lot of activity has been noted in the field of MCSCF theory (Olsen and Yeager 1983). The main thrust of this activity has been towards (i) the development of efficient techniques for solving the 'first order' MCSCF equation (ii) the development of a higher order MCSCF theory e.g. quadratically convergent MCSCF algorithms (QCMSCF). Although considerable progress has been made in the field of QCMSCF theory in recent years, the computational involvement in methods of this category is high enough to discourage large scale practical applications of the algorithm and even now the bulk of MCSCF calculations are based on the first order variational equation only.

Over the last few years we have developed and successfully applied in our laboratory a novel technique for solving the first order MCSCF equation (Mukherjee 1978; Adnan *et al* 1978; McWeeny and Newbould 1980; Bhattacharyya and Mukherjee 1981). The one-configuration analogue, too, has been widely tested (Bhattacharyya and Mukherjee 1979; Bhattacharyya *et al* 1982; Das *et al* 1984). The method has many desirable features e.g. smooth and fast convergence, numerical stability, ease of programming, etc. Even then, in the course of pursuing our research programme on the calculation of ground and excited state potential surfaces of small carbonyls and thiocarbonyls (Das *et al* 1986) at the INDO/2-MCSCF level, we felt that we should look for some means of accelerating the approach to self-consistency within the framework of our method even though it outperforms many of the currently used techniques of solving the first order MCSCF equation in its improved rate of approach to self-consistency. This becomes imperative just for cutting down the total computational expenses when large scale applications are envisaged. The present paper describes our experience with two such means of convergence acceleration employed by us. Besides, we present here the energy-optimized geometrical parameters of the simplest nitrosyl molecule viz, HNO in the ${}^{1,3}n\pi^*$ state, the final state electron densities and dipole moment. The outlay of this paper is as follows: §2 discusses the general conditions of stationarity and in §3, the algorithm used by us is derived in a slightly different way. The convergence acceleration schemes are proposed in §4 while §5 presents the results.

2. General condition of stationarity

Let us consider a truncated set of n molecular orbitals (MO) $\Phi = \{\phi_1, \phi_2, \dots, \phi_i, \dots, \phi_n\}$ which are linear combinations of a set of m -basis functions ($m \geq n$), $\chi = (\chi_1, \chi_2, \dots, \chi_i, \dots, \chi_m)$ are related by the linear transformation:

$$\Phi = \chi T, \quad (1)$$

where T is an $(m \times n)$ matrix of the linear expansion coefficients. The variational trial function $\tilde{\psi}$ is given by:

$$\tilde{\psi} = \sum_{I=1}^N C_I \psi_I, \quad (2)$$

where the ψ_i 's are Slater determinants (with appropriate spin couplings) constructed

from the set $\Phi = \{\phi_1, \phi_2, \dots, \phi_n\}$ and the corresponding energy functional is

$$\begin{aligned}\tilde{E} &= \langle \tilde{\psi} | H | \tilde{\psi} \rangle / \langle \tilde{\psi} | \tilde{\psi} \rangle \\ &= \sum_{ij} (P_1)_{ij} \langle \phi_i | h | \phi_j \rangle + \frac{1}{2} \sum_{ijkl} (P_2)_{kl,ij} \langle kl | ij \rangle,\end{aligned}\quad (3)$$

where P_1 and P_2 are the one- and two-electron density matrices respectively. If we now proceed to make $\tilde{E}$ stationary with respect to variations in (i) the ci coefficients $\{C_i\}$ and (ii) the orbitals, through variations δT in the linear expansion coefficients T_{ij} , we get two sets of coupled equations. Stationary conditions for the first type of variations leads to the normal ci equation

$$HC = CE, \quad (4)$$

while the condition for the stationarity with respect to variations of the type (ii) subject to the orthonormality of the orbitals, is expressed in the form

$$hTP_1 + Z = ST\varepsilon \quad (5)$$

where ε is the matrix of Lagrangian multipliers arising from the orthonormality constraints, and Z represents the electron-electron repulsion matrix with elements defined by

$$Z_{pi} = \sum_{jkl} \sum_{qrs} T_{jq}^\dagger \langle pq | rs \rangle T_{rk} T_{sl} P_{2kl,ij}.$$

One can easily show that the necessary and sufficient conditions for a given set of orbitals $\phi (= \chi T)$ to satisfy (5) is that ε must be hermitian. A variety of methods has been suggested for achieving this condition. The method adopted by us for solving (5) proceeds as follows in the next section.

3. Determination of MCSCF orbitals

Let us start by noting that the equation to be solved is $V = ST\varepsilon$ where

$$V = hTP_1 + Z, \quad (6)$$

and

$$V^\dagger = \varepsilon^\dagger T^\dagger S. \quad (7)$$

Multiplying (6) by $T^\dagger$ from the left and (7) by T from the right we have (see Mukherjee 1978):

$$T^\dagger V = (T^\dagger ST)\varepsilon = \varepsilon; \quad (T^\dagger ST = 1), \quad (8)$$

and

$$V^\dagger T = \varepsilon^\dagger (T^\dagger ST) = \varepsilon^\dagger. \quad (9)$$

Combining (9) with (8) we have (noting that $TT^\dagger = S^{-1}$)

$$\varepsilon^\dagger \varepsilon = (V^\dagger T T^\dagger V)$$

The stationarity condition demands that

$$\varepsilon^\dagger = \varepsilon,$$

so that at convergence

$$\varepsilon^\dagger \varepsilon = \varepsilon^2 = (V^\dagger S^{-1} V),$$

i.e.

$$\varepsilon = (V^\dagger S^{-1} V)^{1/2}.$$

Away from the stationary point (12) provides an 'estimate' of the ε matrix ($\tilde{\varepsilon}$, say). At the n th iterative stage (7) with ε replaced by $\tilde{\varepsilon}$ reads as follows:

$$V_n = S T_n \tilde{\varepsilon}_n,$$

or,

$$T_n = S^{-1} V_n \tilde{\varepsilon}_n^{-1} = S^{-1} V (V^\dagger S^{-1} V)^{-1/2}.$$

At the true stationary point $\varepsilon^\dagger = \varepsilon$ and (13) does not update the coefficient matrix T further—otherwise, the right hand side of (13) provides an updated coefficient matrix. This leads us to the following iterative sequence for the self consistent determination of T (or ϕ):

$$T_n \rightarrow T_{n+1} = S^{-1} V_n (V_n^\dagger S^{-1} V_n)^{-1/2}.$$

If $\varepsilon^\dagger = \varepsilon$ within a preassigned limit, iterations are terminated (a corresponding check can also be made on the electronic energy itself).

4. Convergence acceleration

Any iterative scheme for solving (5) would converge (when it does) at a rate guided by the structure of the algorithm itself. We may call it the 'intrinsic convergence characteristic' which is found to be very good for the present method. However, the determination of MCSCF wavefunction requires solution of the CI equation (4) and equation (5) as coupled tasks and convergence is found to be very slow with many of the available techniques for solution of (5). Normally, one resorts to sophisticated damping and interpolation techniques to achieve fast and smooth convergence. One wonders whether the adoption of a 'convergence-aid' of this kind could improve the efficiency of our algorithm further. In what follows we present our findings in this respect.

4.1 An interpolation scheme

An interpolation method based on direct inversion in the iterative subspace (Pulay 1980, 1982; Csazar and Pulay 1984) has been shown to enhance the rate of approach to self-consistency in one-configuration SCF calculation, the enhancement being particularly noticeable in the quadratic region. Surprisingly, the method, in spite of the promise it holds out, has never been applied in the context of MCSCF calculation. To adapt the DIS procedure to the framework of our algorithm for solving the CI equation we have to define first a suitable error vector (e_i) at the i th stage of the iterative process. This vector should be a faithful measure of the 'distance' of the MCSCF wavefunction

in the i th iteration from the converged solution. The most natural choice would be to take

$$e_i = \varepsilon_i - \varepsilon_i^\dagger = [T^\dagger V_i - V_i^\dagger T_i], \quad (15)$$

since $\varepsilon_i^\dagger = \varepsilon_i$ at convergence, $e_i \rightarrow 0$ (null vector) as iterations proceed to self-consistency. One can safely assume that the changes in the MCSCF orbitals in two consecutive iterations ($i, i+1$) are *small in the quadratic* region. Therefore, the error vector e_i at the i th iterative stage may be taken to be a linear function of the parameters $\{\beta_{pq}\}$ characterizing the trial wavefunction. One can then search for a linear interpolation of the consecutive parameter vectors as follows:

$$\tilde{\beta} = \sum_i a_i \beta^i. \quad (16)$$

The linear interpolation in (16) should be such that the corresponding linear interpolation of the consecutive error vectors ($e_1, e_2, \dots, e_i, \dots$) approach the null vector as closely as possible i.e.,

$$\tilde{e} = \sum_i a_i e_i = 0 \quad (17)$$

Obviously, (17) can be satisfied only in the least squares sense. Thus minimizing the norm of $\tilde{e}$ with a suitable defined metric subject to the constraint

$$\sum_i a_i = 1, \quad (18)$$

we arrive at the following set of linear simultaneous equations to be solved for the determination of the interpolation coefficients $\{a_i\}$

$$\begin{bmatrix} b_{11} & b_{12} & \dots & b_{1n} & 1 \\ b_{21} & b_{22} & \dots & b_{2n} & 1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ b_{n1} & b_{n2} & \dots & b_{nn} & 1 \\ 1 & 1 & \dots & 1 & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \\ \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \quad (19)$$

where λ is the Lagrangian multiplier that takes care of the constraint (18), $b_{ij} = \text{Tr}(e_i e_j^\dagger)$. Once the coefficients $\{a_i\}$ are known we can determine the interpolated orbitals T (or any other parameter vector suitably chosen) as follows:

$$\tilde{T}_{n+1} = \sum_{i=1}^n a_i T_i.$$

In practice, however, such an interpolation is not entirely suitable as it does not preserve the orthonormality of T . Instead, it is better to perform the interpolation on the MCSCF operator (matrix) V itself as follows

$$\tilde{V}_{n+1} = \sum_{i=1}^n a_i V_i.$$

A similar scheme has been successfully adopted in one-configuration work (Pulay

4.2 A damping technique

Since its introduction by Hartree, the use of damping of some kind or the other has been quite common in SCF or MCSCF calculations. What we have adopted in the course of our calculations is essentially a kind of Hartree damping applied to the Fock operator V directly. Let V_{i-1} and V_i be the MCSCF operator (matrix) in $i-1$ and i consecutive iterations. The updating of the orbitals (coefficient matrix T) is then done after replacing V_i by $\tilde{V}_i$ where

$$\tilde{V}_i = V_{i-1}(1 - \lambda) + \lambda V_i \quad (0 < \lambda \leq 1).$$

The conventional undamped iteration scheme corresponds to the choice $\lambda = 1$. λ should be restored as soon as the iterations move into the quadratic region. Otherwise the descent rate becomes too slow. To judge whether damping should be withdrawn or continued, one should ideally calculate $(\partial^2 E_i / \partial \lambda^2)$ at that particular iterative step. If $(\partial^2 E_i / \partial \lambda^2) > 0$ damping is continued, and otherwise withdrawn.

5. Results and discussion

5.1 Relative performance of the convergence acceleration scheme (damping version)

The analysis has been carried out with H_2CO and HNO molecules in the $1^3\pi\pi^*$ states. The trial wavefunction ($\tilde{\psi}$) is of the form

$$\tilde{\psi} = \frac{1}{\sqrt{2}} [|\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_j \dots \phi_n \bar{\phi}_n| \pm |\phi_1 \bar{\phi}_1 \dots \phi_j \bar{\phi}_i \dots \phi_n \bar{\phi}_n|]$$

so that only the orbital forms are to be varied, CI coefficients being symmetrically determined. The molecules are taken in their respective ground state equilibrium geometries as calculated under the standard INDO/2 approximations. The calculations, too, are carried out at the same level of approximation (viz INDO/2).

Table 1 displays convergence profiles for H_2CO in the $1^3\pi\pi^*$ states for (i) undamped iterations (ii) damped iterations (iii) iterations with interpolation done under the DIIS procedure. In each case, the iterations were started with the ground state vectors. The convergence criterion was set equal to 10^{-5} a.u. in energy. The damping factor was chosen to be equal to 0.75 and was introduced right at the beginning. The damping was withdrawn when $\Delta E = |E_{n+1} - E_n| \leq 0.0002$ a.u., subject to at least 10 iterations being carried out. These parameters were determined through a number of exploratory calculations and were later found to be more or less optimal for different systems. The DIIS procedure saved additional computational labour required to compute $(\partial^2 E_i / \partial \lambda^2)$ to decide the point of withdrawal of damping. The DIIS procedure was switched on only after 10 iterations. A perusal of table 1 clearly indicates that although convergence was achieved in all the cases, the fastest convergence was achieved with damped iterations. The DIIS procedure is found to be ineffective so far as acceleration of convergence is concerned. Moreover, the DIIS procedure suffers from a severe ill-conditioning

Table 1. MCSCF convergence profiles in (i) unaided (ii) damped (iii) interpolated (by DIIS) iterations (convergence criterion $\epsilon = 10^{-5}$ a.u.). The system is H_2CO in $^1n\pi^*$ state.

Number of iterations	Electronic energy (a.u.)		
	Without damping	With damping	With DIIS*
0	-42.885845	-42.885845	-42.885845
1	-42.899554	-42.899554	-42.899554
2	-42.908499	-42.908499	-42.908499
3	-42.915320	-42.917523	-42.915326
4	-42.920630	-42.925188	-42.920630
5	-42.924665	-42.929959	-42.924665
6	-42.927694	-42.932496	-42.927694
7	-42.929915	-42.933646	-42.929915
8	-42.931517	-42.934046	-42.931517
9	-42.932653	-42.934246	-42.932653
10	-42.933447	-42.934809	-42.933447
11	-42.933996	-42.935008	-42.933996
12	-42.934372	-42.935111	-42.934372
13	-42.934628	converges at 14th iteration	-42.934519
14	-42.934800		-42.934665
15	-42.934916		-42.934777
	converges at 21st iteration		converges at 21st iteration

* DIIS procedure switched on after 10 iterations.

of the DIIS procedure (Pulay 1980) in SCF calculations with the traditional repeated diagonalization scheme. It may be that a different choice error vector would be more appropriate for our method. The same conclusion could also be drawn from the calculation on the $^3n\pi^*$ state of H_2CO .

In table 2 convergence parameters for the damped and undamped iterations in MCSCF calculations performed on the $^{1,3}n\pi^*$ states of H-N-O are displayed. The damping parameters are just the same as used in the case of H_2CO . The case of HNO is particularly interesting as it provides us with a typical example of a slowly converging

Table 2. Convergence parameters obtained in MCSCF calculations on the $^{1,3}n\pi^*$ states of HNO with and without damping.

Molecule	Electronic state	Number of iterations required for convergence	
		With damping	Without damping
HNO	$^1n\pi^*$	29	44
	$^3n\pi^*$	28	38

Damping parameter $\lambda = 0.75$ and convergence criterion

MCSCF iterations within the framework of our method. A perusal of table 2 clearly indicates the efficacy of the simple Hartree type of damping in MCSCF calculations. It also proves that the damping parameters chosen by us are system independent and are more or less optimal although minor variations from system to system can not be ruled out.

5.2 Properties of HNO in $1,3n\pi^*$ states

In table 3 we present the fully optimized geometrical parameters of HNO in the ground and $1,3n\pi^*$ states. Experimental or *ab initio* theoretical data have been included in the table wherever such data are available. Our computed results are in fairly good agreement with these results. One interesting point is the predicted opening of the H-N-O angle in the $3n\pi^*$ state and the narrowing of it in the $1n\pi^*$ state with respect to the corresponding angle in the ground state. Similarly, increase in the computed N-O bond length is slightly larger in the $1n\pi^*$ state than in the corresponding triplet.

In table 4 the computed net charges on different atoms of HNO in the ground and $1,3n\pi^*$ states at the respective equilibrium geometry are displayed. The calculated net dipole moments are also given. There appears to be a significant increase in the dipole moment following $n \rightarrow \pi^*$ transition. Experimental data, however, is not available for confirming this prediction. Studies in photochemical reactions of this molecule and related species at the INDO/2-MCSCF level are under way.

Table 3. Equilibrium geometrical parameters in the ground and $1,3n\pi^*$ states of HNO as computed by MCSCF-INDO/2 calculations.

Molecule	Electronic state	Computed geometrical parameters		
		rN-H(Å)	rN-O(Å)	H-N-O (Degrees)
HNO	$1A'$ (Ground)	1.090 [1.063] ^a	1.190 [1.212] ^a	111.2 [108.6] ^a
	$1A''$ ($1n\pi^*$)	1.075 [1.06] ^a	1.218 [1.21] ^a	107.1 [108.5] ^a
	$3A''$ ($3n\pi^*$)	1.072 [1.03] ^b	1.205 [1.24] ^b	115.3 [116.7] ^b

Bracketted quantities refer to experimental or *ab initio* theoretical results.

^a Experimental results (Dalbey 1958); ^b Theoretical results (Bruna and Marian 1979; Momura 1980).

Table 4. Computed net charges on different atoms in the ground and $1,3n\pi^*$ states of HNO. Calculated dipole moments in these states are also included (calculations refer to equilibrium geometry in each state).

Molecule	State	Computed net charges on different atoms			Dipole moment (Debye)
		H	N	O	
HNO	$1A'$	0.0169	0.0970	-0.1138	1.487
	$1A''$	0.1147	-0.0496	-0.0651	1.823
	$3A''$	0.1124	-0.0323	-0.0801	1.806

6. Conclusions

The INDO/2-MCSCF calculations appear to be quite useful for studying molecular geometry in excited electronic states. The algorithm used by us for solving the MCSCF equation is fast. The speed of convergence can, moreover, be significantly improved by using a simple damping technique. The DMS procedure when coupled to our algorithm proved to be ineffective.

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Linked-cluster theorem in open shell coupled-cluster theory for mp - mh model space determinants

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Abstract. In this paper we have demonstrated the following aspects of the open-shell coupled cluster (CC) theory when the model space consists of mp - mh determinants: (i) If no other subsidiary conditions (besides the 'minimality' requirement $PSP = 0$) on the normalization of the wave functions are imposed, then the demand that the waveoperator admits of the core-valence separation of energy is inconsistent with the assumption of intermediate normalization. Thus all the discussions on the appearance of unlinked diagrams based on the implicit use of intermediate normalization are invalid. (ii) The open-shell CC developments of Mukherjee *et al* are independent of the normalization of the wavefunctions and the linked cluster theorems and the core-valence separation derived by them are valid for mp - mh model space functions. In particular it has been shown that there are two different cluster ansatz for which the aspect (ii) above is valid. For a valence-universal wave operator Ω admitting of a core-valence separation, it has been proved that the CC equations are linked as a consequence of the multicommutator nature of the expressions. There is a choice between two alternative schemes: one in which S operators connecting all the kp - kh determinants with $k < m$ and $k > m$ are retained, and another in which transitions for $k < m$ are ignored. For a normal ordered cluster ansatz for Ω , one has a linked expression if the subsystem embedding condition (SEC) is adhered to. Here coupling of all the kp - kh determinants to the model space has to be retained if we wish to decouple the various valence sectors of the Hilbert space.

Keywords. Many-body theory; open-shell theory; coupled-cluster theory.

1. Introduction

There has been extensive development of the open-shell coupled cluster theory over the last decade as a viable method for treating electron correlation, and it now appears that it may finally become competitive in its range of applicability with the configuration interaction technique without, however, the limitation of size-inconsistency (see e.g., Dykstra 1984). In so far as one may view the coupled-cluster (CC) approach as a complement of perturbation theory, involving summation of classes of terms up to infinite order, it seems worthwhile to analyse the efficacies of the coupled-cluster approach vis-a-vis the perturbation theory. Both the open-shell coupled cluster theory and the open-shell perturbation theory start with the partition of the N -electron Hilbert space into a model space (characterized by the projector P) and the virtual space complement (characterized by the projector Q), and develop expansion of a set of the exact eigenfunctions around starting functions in the model space. The coupling

of the Hamiltonian to generate an effective Hamiltonian H_{eff} which acts only on the model space and furnishes the exact eigenvalues. It is generally believed that one needs a 'complete' valence model space—amounting to inclusion of the determinants corresponding to all possible ways of allocating electrons in the valence orbitals, to prove the linked cluster theorem for energy. Thus, Brandow (1967) and Lindgren (1974) discuss the consequences of choosing a complete valence model space in generating the linked diagram expansion of energy in the framework of the open-shell perturbation theory. Lindgren (1978) and Jeziorski and Monkhorst (1981), base their proof of the linked cluster theorem in the context of open-shell coupled cluster theory quite essentially on a choice of complete valence model space. In contrast, the development of the coupled cluster theory of Mukherjee and coworkers (Mukherjee *et al* 1975, 1977a, b; Mukherjee 1979; Haque and Mukherjee 1984a) uses model spaces that are somewhat more general than those considered above and the proof of the linked-cluster theorem rests on either a hierarchical generation of the wave-operator for various m valence model spaces, starting at the zero valence level (called the 'subsystem embedding condition' (SEC) (Mukherjee, 1979; Haque and Mukherjee 1984a), or a Lie-algebraic structure of the CC equations, or a combination of both.

Recently Brandow (1983) pointed out that the linked-cluster theorem breaks down in the context of perturbation theory when there are both valence holes and valence particles in the model space and one intuitively takes the space spanned by all the $mp-nh$ determinants with m valence particles and n valence holes as constituting the model space. For $m = n$, the situation is tricky: Brandow, in particular, discusses a disturbing situation where one takes all the $h-p$ determinants in the model space and finds that there are unlinked terms in H_{eff} coming through a coupling of these determinants with the vacuum Φ_{HF} even at the second order. Thus the vacuum interacts with the model space functions and there is a breakdown of the apparently well-established 'core-valence separation' (Brandow 1967). Ways to overcome this difficulty within the framework of open-shell perturbation theory are (i) to use either incomplete model spaces (taking, for example, the function Φ_{HF} itself in the model space) as done by Haque and Mukherjee (1984b) or (ii) to use an expanded model space which involves determinants corresponding to all possible occupancies of *electrons* (rather than hole-particle occupancies) in the valence orbitals. In the choice (i), there are usually disconnected diagrams (Hose and Kaldor 1979, 1980; Haque and Mukherjee, 1984b) and the choice (ii) utilizes a very large model space which may be computationally cumbersome and is also potentially ill-conditioned because of the intruder state problem (Schucan and Weidenmüller 1972, 1973). This situation persists in the open-shell coupled cluster development of Lindgren (1978) and Jeziorski and Monkhorst (1981). The purpose of this paper is to show that this problem is nonexistent for the approaches of Mukherjee *et al* (1975, 1977a, b) and Haque and Mukherjee (1984a). In particular, we shall prove, utilizing two different cluster ansätze, that one can completely separate the calculation of the vacuum energy from the open-shell calculations in a linked manner, and there is always a core-valence separation, even in the case of $mh-mp$ determinants as constituting the model space. Thus the energy differences form a linked series. The development is particularly simple when a valence-universal wave-operator of the form $\exp(S)$ is used for all the $mp-mh$ sectors of the Hilbert space (Mukherjee *et al* 1975, 1977a, b). When a normal ordered ansatz $\{\exp(S)\}$ of the wave-operator is used, the situation is somewhat more subtle, and one may show that the intermediate normalization breaks down in this case, although H_{eff} is still

linked. It appears that the manipulations of the Bloch (1958) equation by Lindgren and Jeziorski and Monkhorst implicitly assumed the intermediate normalization condition even for the incomplete model space, and this is the reason behind their arriving at an unlinked series. In contrast, the treatment of Mukherjee and coworkers does not depend on this assumption, though it should be said in all fairness that this aspect had not been recognized by them earlier.

2. Core valence separation for model spaces containing valence holes and valence particles

2.1 General consideration

Let us assume that we have a set of model space functions comprised of the complete set of $mp-nh$ determinants obtained by assigning m particle and n hole occupancies among the active particle and hole orbitals. As the Hamiltonian H does not conserve the number of hole or particle occupancies separately, this model space couples generally with all the other $m'p-n'h$ determinants satisfying the relation $m-n = m'-n'$. The additional complication for valence holes arises precisely due to the presence of this coupling.

In particular, when $m = n$, all the $m'p-m'h$ determinants are coupled together, including the vacuum function Φ_{HF} itself ($m' = 0$), and the demand of core-valence separation presupposes that the wave-operator Ω must contain all possible excitations out of Φ_{HF} itself quite independent of other operators. Thus we have the curious situation that an Ω satisfying core valence separation must have not only the regular excitations for $mp-mh$ determinants in the model space to virtual space functions including Φ_{HF} , but also the reverse excitation from Φ_{HF} to the model space functions themselves. The combined effect of these two types of excitations will then, in general, lead to terms in Ω which cause scattering within the model space and the assumption of intermediate normalization breaks down! As, in the usual development of open-shell many body theories, the intermediate normalization convention is almost always made use of, many workers start out with expressions valid for intermediate normalization which ceases to be true when $mp-mh$ determinants constitute the model space and conclude that there are unlinked terms in this case.

The starting point in all the developments of open-shell many-body theories is the so-called Bloch equation (Bloch 1958):

$$H\Omega P = \Omega H_{\text{eff}} P. \quad (1)$$

If intermediate normalization (i.e. $P\Omega P = P$) is assumed, then

$$QH\Omega P = Q\Omega PH_{\text{eff}} P \quad (2)$$

and

$$PH\Omega P = PH_{\text{eff}} P. \quad (3)$$

We want to prove that with $mp-mh$ determinants in the model space there are unlinked terms in H_{eff} when (4) is used to generate H_{eff} . The unlinked terms discussed by Brandow (1983) originated from the use of (3) for H_{eff} .

Let us assume that we consider in addition to the functions in the model space, other $m'p-n'h$ (with $m', n' \leq m$) functions as constituting lower valence rank model space. We want to consider all these model spaces simultaneously (Mukherjee *et al* 1977a; Haque and Mukherjee 1984a), because only by considering all these model spaces together can we get around the 'redundancy problem' associated with the cluster amplitudes of Ω (Mukherjee *et al* 1977a, b; Haque and Mukherjee 1984a; Pal *et al* 1977). According to Kutzelnigg (1982, 1984) and Kutzelnigg and Koch (1983) this is a 'Fock space formulation'. The core-valence separation will now be proved for two different choices of the cluster-ansatz for Ω . We shall show that there are two distinct ways of achieving this, each appropriate for one particular choice of Ω .

2.2 Use of valence-universal Ω with core-valence separation

We assume that our wave-operator Ω is of the form (Mukherjee *et al* 1977; Mukhopadhyay *et al* 1979):

$$\Omega = \exp(T) \exp(S),$$

acting on the starting functions Ψ_{0l}^{mp-mn} , where T corresponds to the cluster amplitudes of the vacuum problem:

$$\psi_{gr} = \exp(T) \Phi_{\text{HF}}$$

We also assume that these T amplitudes have been solved. The Schrödinger equation for the $mp-mh$ model space problem may be written as

$$H \psi_l^{mp-mh} = E_l^{(m)} \Psi_l^{mp-mh}$$

Introducing the "dressed" Hamiltonian $\bar{H}$ through

$$\bar{H} = \exp(-T) H \exp(T)$$

and separating the ground state energy E_{gr} from $\bar{H}$ as

$$\bar{H} = \tilde{H} + E_{gr} = \tilde{H} + \langle \Phi_{\text{HF}} | \bar{H} | \Phi_{\text{HF}} \rangle,$$

we have

$$\begin{aligned} \tilde{H} \exp(S) \Psi_{0l}^{mp-mh} &= (E_l^{(m)} - E_{gr}) \exp(S) \Psi_{0l}^{mp-mh} \\ &= (\Delta E_l^{(m)}) \exp(S) \Psi_{0l}^{mp-mh} \end{aligned}$$

Thus, provided we are interested only in "energy differences" ΔE_l , core-valence separation is guaranteed through the multiple cluster ansatz (5) for Ω .

If we impose in addition the condition that Ω is valence-universal in the sense that it correlates also all the lower valence $m'p-n'h$ (with $m', n' < m$) sectors of the Hilbert space, then there is no redundancy problem, and we may solve for the S cluster-amplitude

Equation (11) clearly shows that for a particular model space characterized by m' , other $kp-kh$ determinants with $k \neq m'$ constitute the virtual space, so that each set of $m'p-m'h$ determinants acts both as virtual space functions and model space functions depending on what model space we have in mind. As the vacuum function is already decoupled from the rest of the functions through the condition

$$\langle \Phi_1^{kp-kh} | \tilde{H} | \Phi_{HF} \rangle = 0 \quad (12)$$

for all $k > 0$,

the modified Schrödinger equation (10) guarantees that eigenvalues of $\tilde{H}$ may be obtained *without considering* Φ_{HF} in the Hilbert space. The multicommutator nature of the operator $\exp(-S)\tilde{H}\exp(S)$ appearing in (11) indicates that the equations determining the cluster amplitudes of S are linked. Also, by projecting on to functions $\Phi_j^{m'p-m'h}$ we have

$$\sum_j \langle \Phi_j^{m'p-m'h} | \exp(-S)\tilde{H}\exp(S) | \Phi_j^{m'p-m'h} \rangle C_{ji}^{m'} = \Delta E_i^{(m')} C_{ii}^{(m')}, \quad (13)$$

where

$$\Psi_{0i}^{m'p-m'h} = \sum_j \Phi_j^{m'p-m'h} C_{ji}^{(m')}. \quad (14)$$

The results discussed above are formally exact, but for connectivity some other additional considerations have been found to be fruitful. Thus, for a transition from a $\Phi_i^{m'p-m'h}$ to another Φ_j^{kp-kh} which involves an *odd* number of 'spectator valence lines', it becomes necessary to introduce S amplitudes corresponding to excitations from $(N \pm 1)$ -electron determinants as well, where N corresponds to number of electrons in Φ_{HF} . For example, for an excitation of the types $\alpha p \rightarrow \alpha \beta rs$ ($\alpha, \beta \in_{HF}$; $p, q, r, s \notin_{HF}$), (11) will look like

$$G_{\alpha p}^{\alpha \beta rs} + G_p^{\beta rs} = 0 \quad (15)$$

where $G_p^{\alpha \beta rs}$ consists of all the connected diagrams involving all the outgoing lines ($\alpha \beta rs$) and incoming lines (αp) in the scattering process, and $G_p^{\beta rs}$ contains all the diagrams in which the open line α does not figure at all. Clearly, if we include in S , operators of the form $\langle rs|s|p\beta \rangle \{a_r^+ a_s^+ a_\beta a_p\}$ (with $\{ \}$ as normal ordering) corresponding to shake-up operators for $(N+1)$ -electron model spaces $a_p^+ \Phi_{HF}$, and demand that $G_p^{\alpha \beta rs} = 0$ separately, then electron affinities can also be simultaneously obtained with excitation energies. Symmetrically, if all operators of the form $\langle \alpha \beta |s| \gamma p \rangle \{a_\alpha^+ a_\beta^+ a_\gamma a_p\}$ are also included, then ionization potentials may also be obtained. In that case, for practical purposes, one may use the approximation that higher rank S operators with spectator lines are zero, as for example the operator $\langle \alpha rs|s| \alpha p \beta \rangle \{a_\alpha^+ a_r^+ a_s^+ a_\beta a_p a_\alpha\}$, and omit the $G_{\alpha p}^{\alpha \beta rs}$ term altogether in (15). In other words, we may use a truncation scheme where S amplitudes for $(N+1)$ -electron problems are used to simulate scattering processes for N -electron problems having a greater number of spectator labels through product operator of the form $(1/n!)S^n$ arising from Ω . Pilot numerical applications of the theory for $mp-mh$ model spaces utilized this version (Mukhopadhyay *et al* 1979), where there are three sets of model space functions (a) $0p-1h$ determinants $\{a_{\alpha HF}^+\}$; (b) $1p-0h$ determinants $\{a_p^+ a_{\alpha HF}\}$ and $1p-1h$ determinants $\{a_p^+ a_{\alpha HF}\}$, so that $m = 1$.

For model spaces involving $2n-2h$ determinants etc., i.e. $m > 1$, the above procedure

transformation (11) indicates that H_{eff} has the following structure:

$$P^{(k)} H_{\text{eff}} P^{(m')} = 0 \text{ for } k \neq m'.$$

Thus H_{eff} is block-diagonal for both $k < m'$ and $k > m'$. This complete block-form is, however, not essential to guarantee that $\Delta E_I^{(m')}$'s are the corresponding differences. A simpler, but equivalent, condition can be that

$$P^{(k)} H_{\text{eff}} P^{(m')} = 0 \text{ for } k > m'$$

which gives H_{eff} in a form that is block-diagonal only along the lower part of the diagonal. Equation (17) implies that we need not include in our S operator excitations out of the $m'p$ - $m'h$ model space to lower valence kp - kh model spaces $k < m'$, but we must have a few equations like (11) with conditions $1 \leq m' \leq m$ and $k > m'$. Note, however, that Ω is then not a wave-operator because it furnishes energies and wave-functions.

2.3 Use of Ω in normal order

We now consider the other form of Ω , which is written in normal order. Lindgren (1979) developed his version of the open-shell cc theory using this ansatz for the Ω operator. The model spaces involving valence particles only. As Lindgren's coupled-cluster equations are well-defined only when one assumes that the same Ω correlates all the lower valence sectors of the Hilbert space (Haque and Mukherjee 1984a; Haque and Mukherjee 1984b, unpublished), a situation similar to the one considered in §2.2 holds good for a normal ordered ansatz for Ω involving valence holes and valence particles. Clearly, to maintain the core-valence separation for mp - mh model space determinants we should include in Ω operators inducing excitation from Φ_{HF} , and as this spells a breakdown of intermediate normalization, Lindgren's working equation will be invalid (compare the discussion of the corresponding perturbative situation by Brandow 1983). Møller (1979) and Haque and Mukherjee (1984a) discussed an alternative mode of operation where intermediate normalization is not used, but instead of solving (2) one solves

$$Q\Omega^{-1}H\Omega P = 0$$

and

$$\Omega P^{-1}H\Omega P = P H_{\text{eff}} P.$$

Clearly, (19) is valid independent of the normalization of Ω . Using the condition that Ω correlates all the $m'p$ - $m'h$ sectors of the Hilbert space, and also that Ω does not correlate amplitudes corresponding to excitations from $(N \pm 1)$ -electron determinants (as was done in §2.2), one may show (Mukherjee 1979; Haque and Mukherjee 1984a) that we have equations

$$Q^{(M)} [\Omega^{(M)-1} \tilde{H} \Omega^{(M)}] P^{(M)} = 0, \text{ for all } M,$$

and

$$P^{(M)} [\Omega^{(M)-1} \tilde{H} \Omega^{(M)}] P^{(M)} = P^{(M)} H_{\text{eff}}^{(M)} P^{(M)},$$

where $\Omega^{(M)}$ is defined by

and diagonalization of $H_{\text{eff}}^{(M)}$ in the M valence model space furnishes the energy differences $\Delta E_I^{(M)}$. The valence rank M is defined by all the possible $n'p-m'h$ model space functions with $n' = (m' \pm 1)$, and m' etc.

The disadvantage with the normal ordered ansatz is that there is no multi-commutator Hausdorff expansion, so that the linked cluster theorem has to be proved in a much more involved manner. The advantage is that the form of Ω is more compact than the ordinary exponential. For model spaces not containing valence holes, this automatically leads to the decoupling of the equations for S amplitudes for various M valence sectors of the Hilbert space (Haque and Mukherjee 1984a). If such a procedure is applied for $m'p-m'h$ model space determinants, then it follows from (20) that we introduce various different transformations to $\tilde{H}$ for getting $H_{\text{eff}}^{(M)}$'s, unlike a single transformation, (11) as in §2.2. Thus, the simplification afforded by modified conditions (16) and (17) are not possible. This is compensated for by the decoupling of the equations for cluster amplitudes for $n'p-m'h$ model spaces with $n' = m' \pm 1$, and m' . This procedure has been followed to generate ionization potential, electron affinity and excitation energy for prototypal π -electron systems by Haque and Mukherjee (1984a).

An alternative procedure, which avoids introduction of scattering amplitudes from $n'p-m'h$ model spaces to the $kp-kh$ determinants with $k < m'$ is to use a single transformation

$$Q^{(M)}\Omega^{-1}\tilde{H}\Omega P^{(M)} = Q^{(M)}\Omega^{-1}\tilde{H}^{(M)}P^{(M)} = 0, \quad (23)$$

rather than (20). This, however, will couple the various M -valence sectors in general and one of the advantages of using the normal order ansatz will be lost.

2.4 SEC And Lindgren's cc equation for $mp-mh$ model spaces

It is instructive to indicate here how SEC can be invoked to generate a linked diagram expansion for energy in Lindgren's formalism in the case of $mp-mh$ model spaces. This will demonstrate two things: (a) the modification necessary to arrive at the linked cluster theorem when valence holes are present and (b) the decoupling between the various $n'p-m'h$ sectors through SEC, which is essential for arriving at a connected series for H_{eff} .

We start out from (1), and find generally, using the normal ordered ansatz that

$$Q\{\bar{H}\bar{\Omega}\Omega\}P = Q\{\bar{\Omega}\bar{\Omega}H_{\text{eff}}\}P. \quad (24)$$

If we consider a particular M valence sector, then it follows that

$$Q^{(M)}\{\bar{H}\bar{\Omega}\Omega\}_M P^{(M)} = Q^{(M)}\{\bar{\Omega}\bar{\Omega}H_{\text{eff}}\}_M P^{(M)}, \quad (25)$$

where $\{\ \}$ denotes normal ordering and $\{\ \}_M$ denotes that the total valence rank of the operator is M . Equation (25) implies that

$$\sum_{i=0}^M Q^{(M)}\{(\bar{H}\bar{\Omega})_{M-i}\Omega_i\}_M P^{(M)} = \sum_{i=0}^M Q^{(M)}\{\Omega_i(\bar{\Omega}H_{\text{eff}})_{M-i}\}_M P^{(M)}, \quad (26)$$

where Ω_i is the i -valence part of Ω . If we invoke SEC, and demand that

$$(\bar{H}\bar{\Omega})_{M-i} = (\bar{\Omega}H_{\text{eff}})_{M-i}, \quad (27)$$

Clearly, to satisfy this for all $M' \leq M$, we must have S operators which transitions from all the M' model spaces to the corresponding virtual spaces; when M corresponds to $mp-mh$ model spaces, all other $kp-kh$ determinants with $k > m$ are part of virtual spaces, and all such transitions must be incorporated into the equations like (28). The various M' valence sectors are necessarily decoupled, however, and (28) is equivalent to (20) derived by Haque and Mukherjee (1984a). Again, as Ω involves excitations from one $m'p-m'h$ space to another $kp-lh$ space and vice-versa, $P\Omega P \neq P$, and instead of (3), we have an analogue of (4):

$$P^{(M)}\{\bar{H}\bar{\Omega}\Omega\}_M P^{(M)} = P^{(M)}\{\Omega\bar{\Omega}\bar{H}_{\text{eff}}\}_M P^{(M)}.$$

Using SEC, we show quite generally that

$$P^{(M')}\{\bar{H}\bar{\Omega}\}_M P^{(M')} = P^{(M')}\{H_{\text{eff}}\}_{M'} P^{(M')} + P^{(M')}\{\bar{\Omega}'\bar{H}_{\text{eff}}\}_{M'} P^{(M')},$$

for all $M' \leq M$

and the linked nature of $\{H_{\text{eff}}\}_{M'}$ can be proved by iteration. Here $\Omega' = 1 - \Omega$.

3. Summary of the main results and concluding remarks

In this paper, we have shown the following things: (a) the demand that one has a complete valence separation when the model space functions are a complete set of determinants is incompatible with the intermediate normalization condition; if other extra constraints are imposed, so that discussions of the linked nature of H_{eff} on expressions derived using tacit assumption of intermediate normalization are invalid; (b) the open-shell coupled cluster theories developed by Mukherjee are independent of the normalization of the wave-functions and the linked cluster theorems derived by them are valid even for $mp-mh$ model space determinants; (c) a valence-universal wave-operator Ω admitting of the core-valence separation has been shown that coupled-cluster equations can be written down which are algebraically linked because of the Hausdorff formula; there is a choice between two alternative schemes: (i) one in which S amplitudes connecting all the $kp-kh$ determinants with $m'h$ determinants with $k \neq m'$ are taken and (ii) the S amplitudes for $k < m'$ are taken; (d) using a normal ordered cluster ansatz for Ω and SEC, connected expressions for determining equations and H_{eff} are obtained; if one insists on a decoupling of the various M valence sectors, then coupling of all $kp-kh$ determinants with $k < m'$ and $k > m'$ are essential.

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Adjoinder

Lindgren has recently developed a cc-theory for a class of restricted model spaces (Lindgren 1985a). A closer look at his formulation, however, reveals that it will involve disconnected diagrams when valence holes are present and when spectator lines are not used to define the cluster-amplitudes (Lindgren 1985b). It can again be shown that the disconnected diagrams do not appear if an intermediate normalization condition is not used.

The strategy that one can use for a general incomplete model space is the following:

(1) We define an m -valence incomplete model space with projector $P^{(m)}$ as consisting of m -valence determinants which are somewhat separated energetically from the other determinants constituting the virtual space $Q^{(m)}$; (2) We introduce m -valence operators $\tilde{S}^{(m)}$ which causes transitions from $P^{(m)}$ to $Q^{(m)}$ space; (3) We invoke *SEC* and demand that the wave-operator $\Omega = \{\exp(\tilde{S})\}$ correlates all the lower valence model spaces as well. These lower k -valence model spaces ($0 \leq k < m$) are spanned by k -valence determinants obtained by deleting $(m-k)$ -valence lines from the m -valence model space functions. (4) We introduce $\tilde{S}^{(k)}$ operators obtained by deleting $(m-k)$ spectator valence lines from $\tilde{S}^{(m)}$ systematically. They are of two kinds: the set $\tilde{S}_{op}^{(k)}$ causes transitions from $P^{(k)}$ to $Q^{(k)}$; the set $\tilde{S}_{cl}^{(k)}$ cause transitions within $P^{(k)}$. The $\tilde{S}_{op}^{(k)}$ amplitudes are determined from the conditions that $Q^{(k)} H_{eff}^{(k)} P^{(k)} = 0$, which also determines $\tilde{S}^{(m)} = \tilde{S}_{op}^{(m)}$, the $\tilde{S}_{cl}^{(k)}$ are determined from the condition that the corresponding $P^{(k)} - P^{(k)}$ matrix-elements of H_{eff} , for which $\tilde{S}_{cl}^{(k)}$ exist, are zero. As there are operators causing

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Cluster expansion of the wave function. Potential energy curves of the ground and excited states of CO

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Abstract. The SAC (symmetry-adapted cluster) and SAC-CI (SAC-configurational interactions) theories have been applied to the calculations of the potential curves of the ground and excited states of the CO molecule. The states studied are valence type $X^1\Sigma^+$, $(4)^1\Sigma^+$, $A^1\Pi$, $I^1\Sigma^-$, $D^1\Delta$, $a^3\Pi$, $a^3\Sigma^+$, $d^3\Delta$, and $e^3\Sigma^-$, and of Rydberg type $B^1\Sigma^+$, $C^1\Sigma^+$, and $F^1\Sigma^+$. For the description of the $X^1\Sigma^+$ and $(4)^1\Sigma^+$ states, we took advantage of the fact that the SAC and SAC-CI solutions satisfy orthogonality and Hamiltonian orthogonality to each other. Near the avoided crossing region of these states, however, the SAC theory fails because of the multi-reference nature of the correlation. Our theoretical potential curves of the ground and various excited states are very similar to the RKR (Rydberg-Klein-Rees) potential curves based on experimental data. The spectroscopic constants calculated also agree well with experimental values.

Keywords. Symmetry-adapted-cluster theory; symmetry-adapted-cluster-configurational-interaction theory; Rydberg and valence excited states; Thouless theorem; non-variational method; coupled-cluster-many-electron theory; quasi-degenerate correlation; Dunham theory; Rydberg and valence transitions.

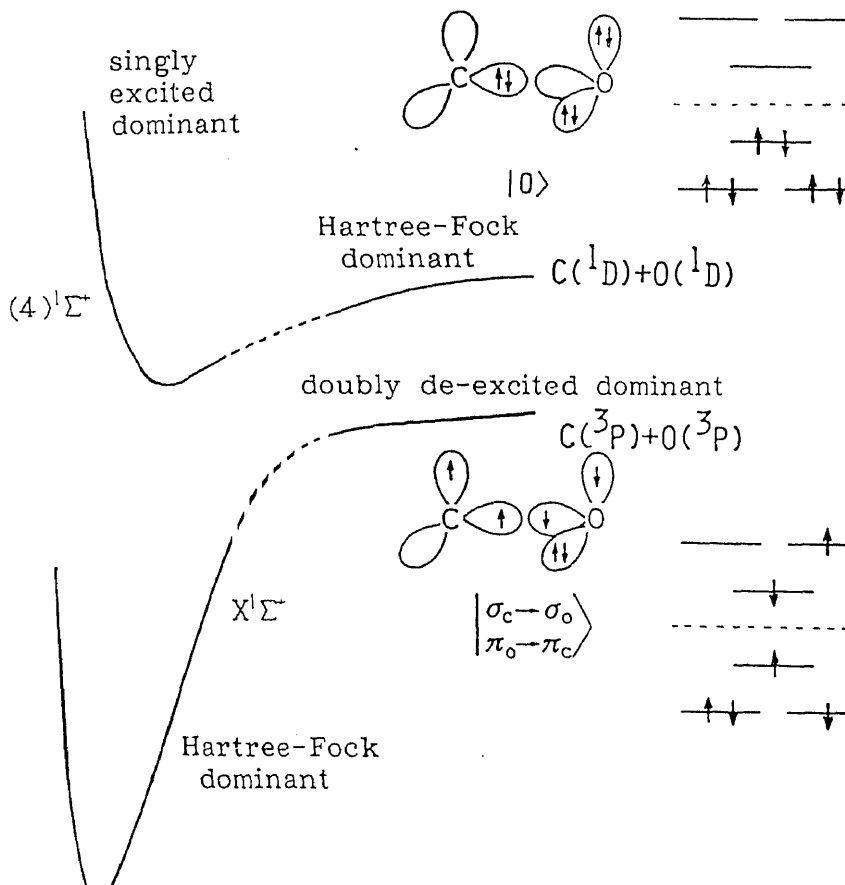
1. Introduction

Adequate description of electron correlation is very important for the study of open-shells and excited states of molecules. This is especially so when we study potential energy curves of the ground and excited states. For this purpose several approaches have been developed, for example, MR (multi-reference)-CI (configuration interaction) (Beunker and Peyerimhoff 1983), MC-SCF (Das 1973; Grein and Banerjee 1975) and cluster expansion (Mukherjee *et al* 1975, 1977; Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978; Paldus *et al* 1978; Mukherjee and Mukherjee 1979; Adnan *et al* 1980, 1982; Haque and Mukherjee 1984). In the cluster expansion approach, the multi-reference type theories are also being developed (Mukherjee *et al* 1975, 1977; Jeziorski and Monkhorst 1981; Nakatsuji 1985) in order to apply to quasi-degenerate states.

In this series of studies, we have developed and applied that SAC (symmetry-adapted-cluster) and SAC-CI theories (Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978). The SAC theory is based on the cluster expansion of the wave function (Čížek 1960; Čížek and Paldus 1971; Bartlett 1981; Paldus 1983) and we usually apply it to the ground state of a molecule. The SAC-CI theory is the CI theory within the sub-space of the SAC wave function (Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978). It has been effectively applied to various kinds of excited and ionized states. (see for example, Nakatsuji 1984, Nakatsuji *et al* 1985, and references therein). The success is basically due to the

orthogonality and the Hamiltonian orthogonality between the SAC and SAC-functions. The linear response theory due to Mukherjee and co-workers (Mukherjee and Mukherjee 1979; Adnan *et al* 1980, 1982; Haque and Mukherjee 1984) seem related incidentally to the SAC-CI theory.

In this paper, we report a calculation of the potential curves of the various excited states of the CO molecule. This molecule is interesting because of the following reasons. In figure 1, we explain intuitively the electronic structures of two $^1\Sigma^+$ states (ground $X^1\Sigma^+$ and $(4)^1\Sigma^+$ states) within the double excitations from the HF (Hartree-Fock) configuration. Near the equilibrium geometry, the HF configuration is a main configuration of the ground state $X^1\Sigma^+$. As the distance increases, the contribution of the HF configuration decreases and finally becomes zero at the dissociation limit. There, the molecule dissociates into the 3P state of oxygen and the 3P state of carbon, i.e., $C(^3P) + O(^3P)$. This state corresponds to a doubly excited configuration from the HF configuration. On the other hand, the $(4)^1\Sigma^+$ state is an ordinary singly excited



essentially as the CO distance increases and finally the HF configuration becomes a configuration near the dissociation limit. There the state is essentially $C(^1D)$ ($O(^1D)$). Thus, the ground state and the $(4)^1\Sigma^+$ state should suffer strong avoided crossing in the intermediate region. We study the potential curves of these states by the HF and SAC-CI theories. We apply the SAC theory to the HF dominant state and calculate the other state by the SAC-CI theory. The basis of the study is the theoretical consistency of these two theories which we discuss in the next section. The other states of the CO molecule studied here, Rydberg excited states $B^1\Sigma^+$, $C^1\Sigma^+$, $F^1\Sigma^+$, and valence excited states $A^1\Pi$, $I^1\Sigma^-$, $D^1\Delta$, $a^3\Pi$, $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$ are essentially singly excited states near equilibrium geometry. They are calculated by the SAC-CI theory.

The potential curves of the CO molecule have been studied by several authors. Neil and Schaefer (1970) reported extensive full-CI calculations within the valence MO's with the minimal STO basis. They explained rough natures of the various excited states, though the crudeness of the basis set may be serious in clarifying the actual system. Ghosh *et al* (1973) applied the equations-of-motion method to several excited states of the CO molecule, with the aid of the experimental potential curves of the ground state. Cooper and Langhoff (1981) reported the MRSD-CI calculation for several states of the CO molecule, using extensive STO basis set. This calculation seems to be the most reliable one so far reported. We have calculated the potential curves of the lower four states (Nakatsuji and Hada 1985), using minimal STO-3G basis, as the test calculation of the multi-reference version of the SAC (Nakatsuji 1985). The MR-SAC calculation reproduced well the full-CI potential curves of the ground and excited states.

SAC and SAC-CI theories

In this section, we briefly explain the SAC and SAC-CI theories. Major emphasis shall be on the non-variational formulation of the theoretical consistency of these two theories. The variational formulation was given before (Nakatsuji 1978, 1979). The SAC wave function for the singlet (ground) state is written as

$$\Psi_{\text{SAC}} = \exp \left[\sum_i C_i S_i^\dagger \right] |0\rangle, \quad (1)$$

$$|0\rangle = \|\psi_1\alpha\psi_1\beta \cdots \psi_i\alpha\psi_i\beta \cdots \psi_n\alpha\psi_n\beta\|. \quad (2)$$

As a reference function $|0\rangle$, we usually adopt a restricted Hartree-Fock solution, but this is not essential because the SAC theory satisfies the Thouless theorem, i.e., the self-consistency (Thouless 1960). The operator $S_i^\dagger$ is a symmetry-adapted excitation operator. A single excitation from occupied orbital i to virtual orbital a is given by

$$S_i^\alpha = \frac{1}{\sqrt{2}} (a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}) \quad (3)$$

where $a_{a\alpha}^\dagger$ and $a_{a\alpha}$ mean the creation and annihilation operators for spin α . The double excitation operators can be written by the products of these excitation operators.

We use a non-variational method to determine the expansion coefficients C_i in (1). We require the Schrödinger equation $(H-E)|\Psi_{\text{SAC}}\rangle = 0$ to be satisfied in the space of

the linked configurations and we get (Nakatsuji 1979)

$$\langle 0 | H - E | \Psi_{\text{SAC}} \rangle = 0$$

$$\langle 0 | S_I (H - E) | \Psi_{\text{SAC}} \rangle = 0.$$

Because the Hamiltonian includes up to two body operators, the energy is calculated exactly from (4) as

$$E_{\text{SAC}} = E_0 + \sum_I C_I \langle 0 | H S_I^\dagger | 0 \rangle + \frac{1}{2} \sum_{IJ} C_I C_J \langle 0 | H S_I^\dagger S_J^\dagger | 0 \rangle.$$

For the excited states, we consider the SAC-CI expansion (Nakatsuji 1978, 1979) and define the configuration function as

$$\Phi_K = R_K^\dagger \Psi_{\text{SAC}}$$

and define the SAC-CI wave function by a linear combination of these configuration functions.

$$\Psi_{\text{SAC-CI}} = \sum_K d_K \Phi_K.$$

In (7) the operators $\{R_K^\dagger\}$ consist of the identity operator $I \equiv R_0^\dagger$ and the symmetry adapted excitation operators. When we consider the excited states which belong to the same symmetry as the SAC solution, the operators $\{R_K^\dagger\}$ are the same as the operators $\{S^\dagger\}$ used in the SAC expansion. With an appropriate choice of the operators $\{R_K^\dagger\}$, we can deal with not only the excited states of different spin-space symmetry, but also ionized and electron attached states (Nakatsuji 1979; Nakatsuji and Hirao 1980). We use the non-variational method to determine the coefficients d_K in (8). Requiring the Schrödinger equation $(H - E) |\Psi_{\text{SAC-CI}}\rangle = 0$ in the space of the linked configurations, we get (Nakatsuji 1979)

$$\langle 0 | H - E | \Psi_{\text{SAC-CI}} \rangle = 0$$

$$\langle 0 | R_K (H - E) | \Psi_{\text{SAC-CI}} \rangle = 0.$$

We note that the SAC and SAC-CI wave functions Ψ_{SAC} and $\Psi_{\text{SAC-CI}}$ satisfy the same set of equations, (4) and (5), and (9) and (10). Especially, when we consider the excited states belonging to the same symmetry as the ground state, the operators $\{R_K^\dagger\}$ represent the same set of the operators as the operators $\{S^\dagger\}$. The solutions of the Schrödinger equation belonging to different eigenvalues are orthogonal to the Hamiltonian. The SAC-CI wave function defined by (8) can represent the ground state wave function as a special case ($d_0 = 1$ and $d_I = 0, I \geq 1$). Therefore, the SAC-CI wave function belonging to different energy from the SAC solution should satisfy

$$\langle \Psi_{\text{SAC}} | \Psi_{\text{SAC-CI}} \rangle = 0$$

$$\langle \Psi_{\text{SAC}} | H | \Psi_{\text{SAC-CI}} \rangle = 0$$

and therefore are important prerequisites for the theory dealing with the properties involving different states (e.g., transition energy, transition moment, etc.).

Computational details

The basis set used in the present calculations is the [4s2p] set of Huzinaga-Dunning (Dunning 1970; Dunning and Hay 1977) for the valence part. For the Rydberg part, diffuse *s* and *p* functions with exponents 0.023 (*s*), 0.021 (*p*) for carbon and 0.032 (*s*), 0.028 (*p*) for oxygen were placed at the nuclear position. The number of the basis set is 100. The HF MO's of the closed-shell system were used as reference MO's for all of the states calculated here. They were calculated by the HONDOG program (King *et al* 1979). The space of the active MO's consists of all the valence and Rydberg orbitals. The number of active MO's is 24.

We applied the SAC method to the HF dominant state and the SAC-CI method to generate the other states. In the short internuclear distance we calculated the ground state by the SAC method and the excited states by the SAC-CI method. At the long internuclear distance we calculated the HF dominant ($4^1\Sigma^+$) excited state by the SAC method. The ground state was calculated by the SAC-CI method as a de-excited state. In the SAC calculations we considered single and double excitations as linked operators and only the products of double excitations (quadruple excitations) in the unlinked terms. We obtain from (5) (Nakatsuji 1979)

$$H_{I0} + \sum_J C_J (G_{IJ} - E_{\text{SAC}} T_{IJ}) = 0, \quad (15)$$

where

$$H_{I0} = \langle 0 | S_I H | 0 \rangle,$$

$$G_{IJ} - E_{\text{SAC}} T_{IJ} = \langle 0 | S_I (H - E_{\text{SAC}}) S_J^\dagger | 0 \rangle + \frac{1}{2} \sum_K C_K \langle 0 | S_I (H - E_{\text{SAC}}) S_K^\dagger S_J^\dagger | 0 \rangle.$$

Equations (6) and (15) were solved iteratively. For closed shells, the solution is equivalent to that of the CCMET (coupled-cluster many-electron theory) (Čížek 1960; Čížek and Paldus 1971). The SAC theory itself is equally applicable to open-shell systems (Nakatsuji 1978; Nakatsuji and Hirao 1978; Hirao and Nakatsuji 1981).

In the SAC-CI calculation, the wave function was truncated at the second order for the coefficients d_K and C_I .

$$\Psi_{\text{SAC-CI}} = \sum_K d_K \left[R_K^\dagger + \sum_I C_I R_K^\dagger S_I^\dagger \right] | 0 \rangle \quad (16)$$

where $C_I = n_{\text{SAC}} C_I$. We include single and double excitations to $R_K^\dagger$ and only double excitations to $S_I^\dagger$. The unlinked terms therefore consist of triple and quadruple excitations. Inserting (16) into (9) and (10), we obtain

$$\sum_L (H_{KL} - E_{\text{SAC-CI}} T_{KL}) d_L = 0, \quad (17)$$

where

$$H_{KL} - E_{\text{SAC-CI}} T_{KL} = \langle 0 | R_K (H - E_{\text{SAC-CI}}) R_L^\dagger | 0 \rangle + \sum_I C_I \langle 0 | R_K (H - E_{\text{SAC-CI}}) R_L^\dagger S_I^\dagger | 0 \rangle.$$

This equation constitutes an eigenvalue problem of a non-symmetric matrix (Hirata and Nakatsuji 1982).

In (16), we renormalized the coefficient C_i by the renormalization factor n_{SAC} of the SAC wave function. This factor was introduced from the following consideration. In the SAC-CI formalism, we calculate the wave functions using an approximate transfer of the electron correlation from the SAC wave function. The SAC wave function is intermediate normalized, taking the weight of the Hartree-Fock part to be unity. On the other hand, the SAC-CI wave function is normalized to unity. Therefore when the electron correlation becomes relatively large, it would be better to transfer the normalized quantity of the electron correlation of the SAC wave function in order to maintain a balance in the SAC-CI wave function. Note however that this modification is rather temporary because the single reference SAC theory itself will breakdown when n_{SAC} is considerably larger than unity (Nakatsuji 1985). Actually in the region of avoided crossing between the $X^1\Sigma^+$ and $(4)^1\Sigma^+$ states, the SAC solution was unstable so that we could not obtain the SAC-CI solution either.

To diminish the size of calculations, we selected the linked operators in the same way as reported before (Nakatsuji 1983). In this calculation the thresholds λ_g and λ_e were set to 1×10^{-5} and 2×10^{-5} au, respectively, for singlet states and λ_e for triplet states was set to 5×10^{-5} au. We included both single and double excitations as main reference configurations used in the selection procedure (Nakatsuji 1983). As the practical dimension to be solved is approximately 1600 at the most. As for the operators included in the unlinked terms, we adopted double excitations whose coefficients in the SD-CI are larger than 5×10^{-3} for SAC and 1×10^{-3} for SAC-CI. The operators in the unlinked terms of SAC-CI consists of single and double excitations whose coefficients in the SD-CI are larger than 8×10^{-2} .

We note that in the present calculations, we include only single and double excitations as the *linked* operators of the SAC and SAC-CI methods. This space is not enough for the description of the $^1\Sigma^+$ valence excited states. Within the present calculations the $(4)^1\Sigma^+$ state is the lowest valence excited state. However, due to the calculations based on the minimal basis sets (O'Neil and Schaefer 1970; Nakatsuji and Hada 1985), there are two other $^1\Sigma^+$ states in the energy region studied here. Our lowest valence excited $^1\Sigma^+$ state is close to the $(4)^1\Sigma^+$ state studied by Cooper and Laidler (1981). Hence, we denoted this state as $(4)^1\Sigma^+$.

4. Potential curves of the CO molecule

The potential curves of the $X^1\Sigma^+$ and $(4)^1\Sigma^+$ states of the CO molecule calculated by the present method are shown in figure 2. For the $X^1\Sigma^+$ state, the curve from 1.5 to 3.5 au was calculated by the SAC method and the curve from 5.0 au to 8.0 au by the SAC-CI method. For the $(4)^1\Sigma^+$ state, we used the SAC-CI method for the curve from 1.5 to 3.5 au and the SAC method for the curve from 5.0 au to 8.0 au.

First we discuss the $X^1\Sigma^+$ state. Since we did not use d -polarization functions

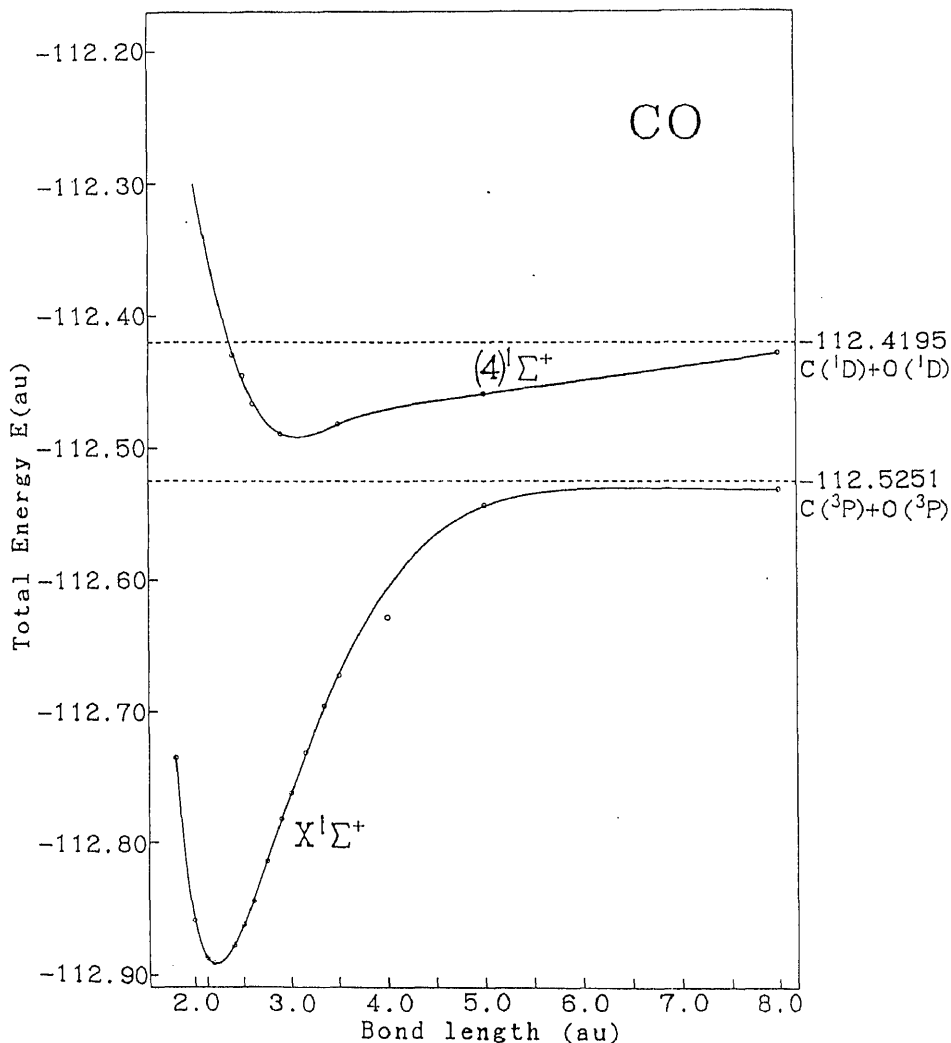


Figure 2. Potential energy curves of the $X^1\Sigma^+$ and $(4)^1\Sigma^+$ states of the CO molecule calculated by the SAC and SAC-Cl methods.

adequate and the potential curve goes through the calculated point at 4.0 au. From the following two reasons we think that the potential curve drawn in figure 2 is better and the point calculated at 4.0 au is out of order.

First is the consideration on the breakdown of the single reference theory. In table 1, we collected the norm of the SAC-NV wave function. A remarkable feature is seen at 4.0 au in the problem. If the single-reference cluster expansion theory is appropriate, the norm of the wave function should not exceed unity by very much. However, at 4.0 au the norm is about 1.2, which is far from the unity. This indicates

Table 1. Norm of SAC-NV wave function of the HF dominant state of the CO molecule

Bond length (au)	norm	Bond length (au)	norm
1.8	1.04	2.9	1.11
2.0	1.05	3.0	1.13
2.132	1.05	3.15	1.16
2.2	1.06	3.35	1.27
2.4	1.07	3.5	1.40
2.5	1.07	4.0	2.49 ^a
2.6	1.08	5.0	1.39
2.75	1.09	8.0	1.17

^aThis value indicates that the result at 4.0 au is unreliable (see text).

that the quasi-degenerate correlation which is not described by the single reference theory occurs in this region of the internuclear separation (Nakatsuji 1985).

The second reason is based on the spectroscopic constants calculated by the different potential curves. We analyzed the potential curves by the Dunham method (Dunham 1932). The results are compared in table 2 where the values given in the second row in parentheses were obtained from the curve going through the calculated point at 4.0 au. The vibrational anharmonicity $\omega_e x_e$ reflects the shape of the potential curve very sensitively. The upper figure in table 2, $\omega_e x_e = 15.7 \text{ cm}^{-1}$ almost reproduces the experimental value, 13.3 cm^{-1} . The same value from the curve going through the calculated point at 4.0 au is 5.48, which is only a half of the experimental value.

Next we discuss the $(4)^1\Sigma^+$ state. Because an appropriate SAC solution is unavailable at 4.0 au, we could not calculate the SAC-CI solution at this point. The potential curve was extrapolated from the reliable curves in shorter and longer internuclear distances. The avoided crossing part is therefore unreliable. We assign this state to the valence $\pi \rightarrow \pi^*$ excitation. No experimental data seems to have been given about this state; for example, see the RKR curves shown in figure 4. Cooper and Langhoff (1972) calculated this state by the MRSD-CI method, so that we compare our spectroscopic results with their results in table 2. The equilibrium bond length r_e is almost the same. Remarkable differences are seen in the term energy T_e and the vibrational anharmonicity $\omega_e x_e$. For the former, our result is lower than theirs by 0.6 eV, and for the latter, our result is almost twice as large as theirs. This is probably due to the inclusion of the linked three and four excitation terms in the present calculation.

In figure 3, we draw all the potential curves calculated with the SAC and SAC-CI method. In figure 4, the potential curves drawn by the RKR method based on the experimental data (Krupenie 1966; Tilford and Simmons 1972) are displayed. The arrow in the upper right corner shows the lower dissociation limit of figure 3. The agreement of the experimental curves and our calculated curves is very good. The theoretical and experimental spectroscopic constants are summarized in table 2. The agreement between the

Table 2. Spectroscopic constants of the ground and the excited states of CO^a.

State			T_e (eV)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
$X^1\Sigma^+$	ground	Calc. ^c	0.0 ^b	1.17	2012	15.7	1.79	0.0184
		Calc. ^d	(0.0)	(1.18)	(1896)	(5.48)	(1.77)	(0.0122)
		Expt.	0.0 ^b	1.13	2170	13.3	1.93	0.0175
$I^1\Sigma^-$	$\pi \rightarrow \pi^*$	Calc.	7.74	1.46	1025	14.5	1.15	0.0173
		Expt.	8.07	1.40	1092	10.7	1.27	0.0185
$D^1\Delta$	$\pi \rightarrow \pi^*$	Calc.	7.79	1.46	1041	13.5	1.15	0.0159
		Expt.	8.17	1.40	1094	10.2	1.26	0.017
$A^1\Pi$	$n \rightarrow \pi^*$	Calc.	7.89	1.29	1390	19.1	1.47	0.0192
		Expt.	8.07	1.24	1518	19.4	1.61	0.0232
$(4)^1\Sigma^+$	$\pi \rightarrow \pi^*$	Calc.	10.89	1.62	795	14.5	0.93	0.0149
		C-L ^e	11.49	1.52	974	7.3	—	—
$B^1\Sigma^+$	$n \rightarrow 3s$	Calc.	10.66	1.14	2070	11.9	1.89	0.0327
		Expt.	10.78	1.12	2113	15.2	1.96	0.0261
$C^1\Sigma^+$	$n \rightarrow 3p_g$	Calc.	11.19	1.15	2252	16.4	1.86	0.0147
		Expt.	11.40	1.12	2176	14.7	1.95	0.0196
$F^1\Sigma^+$	$n \rightarrow 3d_g$	Calc.	12.68	1.13	2059	15.3	1.91	0.0315
		Expt.	(12.37)	(1.15)	(2034)	(198) ^f	(1.86)	—
$a^3\Pi$	$n \rightarrow \pi^*$	Calc.	5.74	1.25	1728	16.9	1.58	0.0181
		Expt.	6.05	1.21	1743	14.3	1.69	0.0190
$a'^3\Sigma^+$	$\pi \rightarrow \pi^*$	Calc.	6.40	1.42	1164	8.01	1.21	0.0104
		Expt.	6.92	1.35	1229	10.5	1.35	0.0189
$d^3\Delta$	$\pi \rightarrow \pi^*$	Calc.	7.18	1.44	1092	7.79	1.18	0.0114
		Expt.	7.58	1.37	1172	10.6	1.31	0.0178
$e^3\Sigma^-$	$\pi \rightarrow \pi^*$	Calc.	7.48	1.45	1089	8.81	1.17	0.0113
		Expt.	7.96	1.38	1118	10.7	1.28	0.0175

^a Experimental values are taken from Huber and Herzberg (1979); ^b dissociation energy is 9.98 eV (calculation) and 11.226 eV (experiment, Krupenie 1966); ^c our final results (see text); ^d calculated values obtained if we assume that the potential curves goes through the calculated point at 4.0 au (see text); ^e theoretical result due to Cooper and Langhoff (1951); ^f this experimental data might be unreliable (see text).

than that of the ground state, and they have a sharp curvature. As seen from the spectroscopic constants shown in table 2, our potential curves reproduce well the experimental results. For the $F^1\Sigma^+$ state, the experimental vibrational anharmonicity $\omega_e x_e$ is extraordinarily large (Krupenie 1966), i.e., 198 cm⁻¹. Our results indicate that this state has the potential curve very similar to the $B^1\Sigma^+$ state, so that this value might be incorrect.

Around the middle left of figure 3, several $\pi \rightarrow \pi^*$ valence transitions are seen. In this region, the states, $^1\Delta$, $^1\Sigma^-$, $^3\Sigma^-$, $^3\Delta$, $^3\Sigma^+$ have the potential minima. These states have the curves of relatively shallow minima. The average internuclear distance of these states is longer than that of the ground state. The singlet pair $D^1\Delta$, $I^1\Sigma^-$ and the triplet

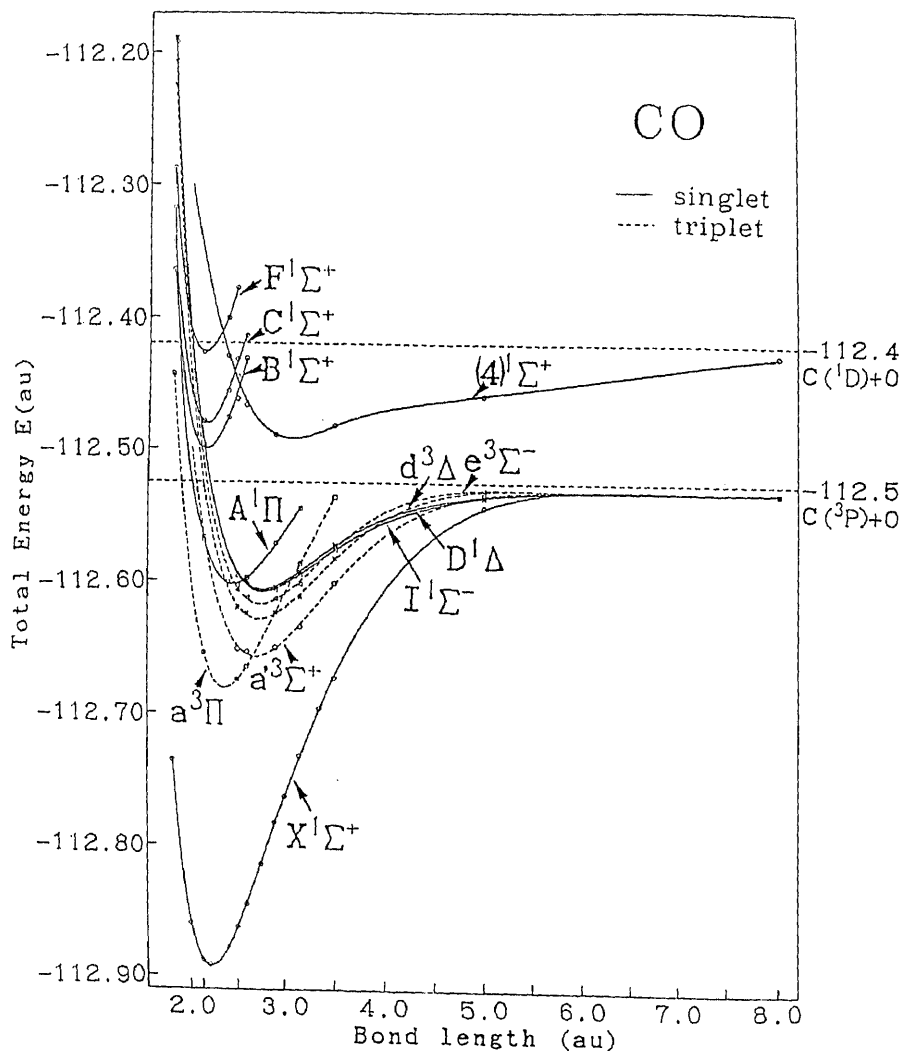


Figure 3. Potential energy curves of the CO molecule calculated by the SAC and s methods.

internuclear region of these potential curves. The reason is as follows. In the pre calculations we considered up to double excitations as *linked* operators. From full-ci study (Cooper and Langhoff 1981), in order to describe these states appropriately at longer internuclear distance it is necessary to include triple and higher excitations in the *linked* operators.

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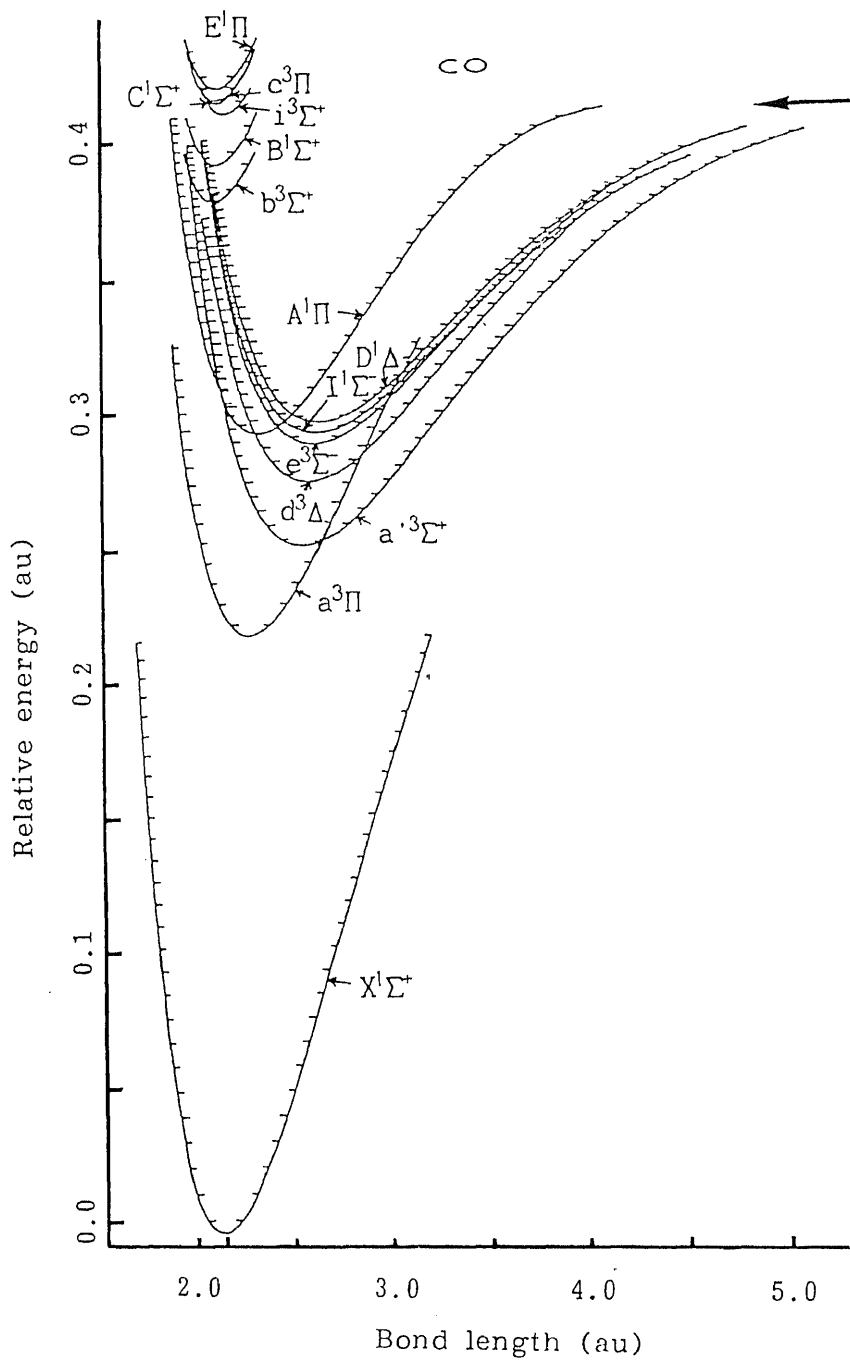


Figure 4. Experimental RKR curves of the CO molecule.

M380, M382, and VP100 computers at the Data Processing Center of Kyoto University. The authors thank these computer centers for the grants of computing time. Part of this study was supported by a Grant from the Japanese Ministry of Education, Science, and Culture.

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The quantum chemistry of valency

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Abstract. It is shown that the chemist's concept of valency can be put in quantum mechanical language. Such a quantification of valency opens up possibilities of new applications which are briefly reviewed. Valency is related to the equilibrium geometry of the molecule through a maximum valency principle. This principle, combined with the idea of molecular orbital valencies, provides a theoretical foundation for the well known Walsh diagrams. Valency can be used as an index of chemical reactivity and valency changes in a reaction can be used to determine the radical nature of intermediates and transition states as well as to indicate the allowed or forbidden nature of reaction paths. Molecular strain may be related to the loss of sigma valency.

Keywords. Valency; maximum valency principle; molecular orbital valency; Walsh diagrams.

1. Introduction

Most theoretical concepts of chemists, like the chemical bond, atomic charge in a molecule, valency, inductive effect and molecular strain, to name only a few, have at best a qualitative basis. The development of quantum chemistry has helped in the quantification of such concepts even though the situation is still far from satisfactory. In this article the highlights of a quantum mechanical treatment of the classical concept of valency attempted by the author's research group is presented. In particular the following topics are discussed:

- (a) The quantum chemical definition of valency and its mathematical properties are presented in §2.
- (b) A 'maximum valency principle' proposed by us recently is discussed, according to which the molecular valency is a maximum at the equilibrium geometry (§3).
- (c) The idea of a valency for each molecular orbital is introduced. This molecular orbital valency is shown to be a measure of the bonding nature of the molecular orbital (§4).
- (d) In §5 we show that the molecular orbital valency can, as a consequence of the maximum valency principle, serve as a quantitative ordinate for Walsh diagrams.
- (e) Valency can also serve as an index of chemical reactivity. It can be used to determine the radical/biradical nature of species. Molecular orbital valency changes in a reaction reflect the allowed or forbidden nature of the reaction path (§6).
- (f) Molecular strain can be quantitatively related to the loss of sigma valency in strained systems (§7).

2. Definition and properties of valency

A quantum chemical definition of valency (Armstrong *et al* 1973; Semenov 1980; Gopinathan and Jug 1983; Jug 1984; Mayer 1985; Natiello *et al* 1985) should desirably have the classical attributes of valency: (a) its value should be close to traditional integer values like 1 for H, 3 for N and 4 for C, (b) it should have a maximum corresponding to the idea of saturation of valency, and (c) it should be a measure of the degree of electron sharing between atoms in a molecule. It has been shown (Gopinathan and Jug 1983) that these properties are satisfied by the following definition of valency:

Valency V_A of atom A is defined as:

$$V_A^{(GJ)} = \sum_a^A \sum_B^B \sum_b^B p_{ab}^2, \quad (1)$$

where P_{ab} is the first order density matrix element between orbital a on atom A and orbital b on atom B . This form of the definition is valid when the basis set orbitals are orthogonal. It can also be defined in a non-orthogonal basis (Mayer 1985; Natiello *et al* 1985). However, it must be realised that definitions of atomic valency in non-orthogonal or different orthogonal bases, even though all formally equivalent, can be numerically different (M S Gopinathan and P Siddarth, unpublished results). This arbitrariness is perhaps unavoidable in any scheme that partitions charge density or its functions into atomic contributions as (1) does. For example, the valency of He in the two-electron system HeH^+ for various types of wavefunctions are (M S Gopinathan and P Siddarth, unpublished results):

- (1) 0.719 for non-orthogonal sto-3G functions
- (2) 0.223 for canonically orthogonalised sto-3G functions
- (3) 0.329 for Schmidt orthogonalised sto-3G functions and
- (4) 0.776 for Löwdin orthogonalised sto-3G functions.

Arguments can be made (M S Gopinathan and P Siddarth, unpublished results) in favour of using the Löwdin orthogonalised wave functions.

Definition of valency for open shell molecules has been controversial (Mayer 1985). We have used (1) for open shell systems also, with $p_{ab} = p_{ab}^\alpha + p_{ab}^\beta$ where p_{ab}^α is the density matrix element for α electrons. Two alternate definitions for open shell systems have been proposed. Thus, Semenov (1980) defines valency as:

$$V_A^{(S)} = \sum_a^A \sum_{B \neq A}^B \sum_b^B p_{ab}^2 + Q_{ab}^2, \quad (2)$$

whereas Mayer (1985) and Natiello *et al* (1985) define it as:

$$V_A^{(M)} = 2 \sum_a^A p_{aa} - \sum_{a,a1}^A p_{aa1}^2, \quad (3)$$

where $\sum_a^A$ means summation over orbitals a on atom A .

Definitions (1) to (3) can be related to the trace of the matrix P^2 which contains all electron-sharing terms, i.e. terms quadratic in bond order. It is then possible to show (M S Gopinathan and P Siddarth, unpublished results) that (a) definition (1) which we have employed in all our studies include all interatomic terms in $\text{tr}P^2$, as it should, since valency measures the extent of electron sharing between atoms, (b) definition (2) implicitly involves the assumption that $2p_{aa}^\alpha \cdot p_{aa}^\beta = p_{aa}^{\alpha 2} + p_{aa}^{\beta 2}$ which is true only for the

sed shell case, and (c) definition includes the number of unpaired electrons on the atom as contributing to valency. A consequence of this is that Mayer's definition (3) gives, for instance, valencies of 3, 4 and 4 for CH_2 , CH_3 and CH_4 species, respectively, whereas our definition (1) would give the values 2, 3 and 4. The latter set of values are closer to the chemist's view and more useful from the point of view of the application of valency as will be evident from the following sections. It may be noted that all three definitions reduce to the same form as (1) for closed shell systems.

For a given definition, valency values are not sensitive to the quality of the wave function at the minimal basis set level. Table 1 shows that valency values obtained using semiempirical and *ab initio* wave functions are very similar. These values are close to the classical integer values in most cases.

Further properties of valency established (Gopinathan and Jug 1983, p. 497) are the

Table 1. Comparison of valency values obtained from different wavefunctions.

Molecule	SINDO ^a	STO-3G ^b	STO-6G ^b
Li_2	1.000	1.007	1.007
N_2	3.000	3.000	3.000
LiH			
Li	0.919	1.000	1.000
H	0.919	1.000	1.000
HF			
H	0.930	0.977	0.974
F	0.930	0.977	0.974
CO			
C	2.57	2.613	2.605
O	2.57	2.613	2.605
H_2O			
H	0.980	0.983	0.981
O	1.960	1.967	1.963
NH_3			
H	0.990	0.989	0.988
N	2.970	2.967	2.964
HCN			
H	0.960	0.990	0.990
C	3.960	3.984	3.983
N	3.000	3.014	3.014
CO_2			
C	3.740	3.966	3.964
O	2.130	2.391	2.388
HCHO			
H	0.890	0.999	0.999
C	3.910	3.966	3.964
O	2.130	2.153	2.150
CH_4			
H	1.000	0.998	0.999
C	4.000	3.993	3.992

^a values from Gopinathan and Jug 1983; ^b values from Ravimohan (1984)

following:

- (a) Valency is invariant to hybridisation of atomic orbitals.
 (b) Atomic valency has the limits:

$$0 \leq V_A \leq \sum_a^A (2q_a - q_a^2), \quad (4)$$

where q_a is the occupancy of the atomic orbital on atom A . This also means that the maximum valency of an atom would be equal to the total number of electrons on it minus the number of core, lone pair and odd electrons on that atom.

The connection between valency and the occupancy of natural orbitals and the eigenvalues of 'bond orbitals' has also been established (Gopinathan and Jug 1983). The definitions of sub- and hyper-valency and the idea of molecular orbital valency will be introduced in later sections.

3. A maximum valency principle

We have recently proposed (Gopinathan *et al* 1986; Ravimohan 1984) a *maximum valency principle* which can be stated as:

'Molecular valency is a maximum at the equilibrium bond angle'. Here molecular valency means half the sum of the atomic valencies:

$$V_M = \frac{1}{2} \sum_A V_A, \quad (5)$$

the factor $\frac{1}{2}$ being introduced to avoid double counting of valencies between pairs of atoms. The principle means, in other words, that molecules assume that shape for which the total valency is a maximum.

Figure 1 gives a plot of molecular valency in H_2O as a function of bond angle. Figure 2 shows the variation of molecular valency in acetylene for symmetric *cis* and

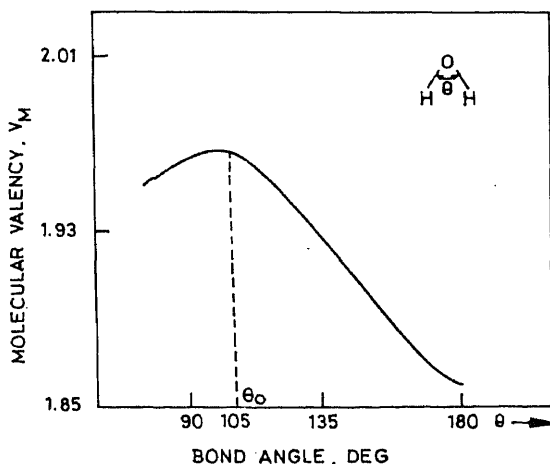


Figure 1. Illustration of the maximum valency principle. Plot of molecular valency in H_2O against bond angle. θ is the equilibrium angle.

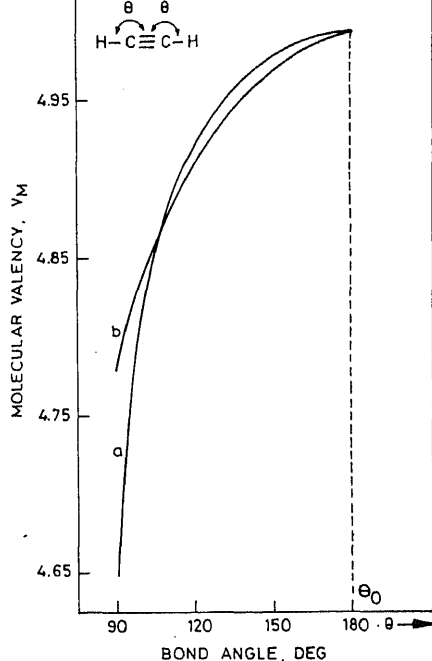


Figure 2. Illustration of the maximum valency principle. Plot of molecular valency in acetylene for (a) symmetric *cis* variation of the HCC angle, and (b) symmetric *trans* variation of the HCC angle.

ans distortions. Clearly in these cases V_M attains its maximum at the equilibrium bond angle. Studies on a variety of molecules have shown (Gopinathan *et al* 1986; Ravimohan 1984) the general validity of the maximum valency principle. However the principle has not been established analytically and efforts are under way towards this end. An important application of the maximum valency principle is that it provides a quantitative ordinate for the famous Walsh diagrams as we describe in §5 below.

Molecular orbital valency

The molecular valency defined by (5) can be decomposed into its molecular orbital (MO) components as (Gopinathan *et al* 1986; Ravimohan 1984):

$$V_M = \sum_i^{mo} v_i,$$

with

$$v_i = \frac{1}{2} \sum_A \sum_a \sum_{B \neq A} \sum_b^{mo} n_i n_j C_{ia} C_{ib} C_{ja} C_{jb}, \quad (6)$$

where n_i is the occupancy of the i th MO, c_{ia} the coefficient of the a th atomic orbital in the i th MO. We call v_i the molecular orbital valency of the i th MO. v_i measures the extent of

sharing of the n_i electrons (1 or 2) in the i th MO among the various atoms, therefore be expected that v_i will be zero for atomic core MO and lone pair MO, unity for strongly bonding MO and will have much smaller values for 'nonbonding' 'antibonding' MO. Extensive comparison (Gopinathan *et al* 1986) of MO v_i with ESCA spectral information as well as Mulliken overlap population analysis has borne this out. Table 2 gives some typical results. The MO valency is thus indeed a quantitative measure of the bonding power of the MO and it can be reliably used for assignment of peaks in the experimental ESCA spectra of molecules.

5. MO valency as ordinate of Walsh diagrams

Walsh diagrams (Mulliken 1942; Walsh 1953; Coulson and Deb 1971; Stenka and Davidson 1973; Buenker and Peyerimhoff 1974) are correlation diagrams of molecular orbital 'binding energies' with molecular geometry. These diagrams have traditionally been used very successfully to explain the shape of molecules. However, Walsh (1953) defines 'binding energies'—the ordinate of the diagram—and his diagrams were based on qualitative arguments regarding atomic overlaps and their relation to

Table 2. Molecular orbital valency (STO-3G results).

Molecule	MO(i)	MO valency v_i	Bonding character of MO* †	
			from v_i	from ESCA
N ₂	1 σ_g	0.004	<i>n</i>	
	1 σ_u	0.000	<i>n</i>	
	2 σ_g	0.849	<i>s</i>	
	2 σ_u	0.000	<i>n</i>	<i>n</i>
	1 π_u	1.000	<i>s</i>	<i>s</i>
	3 σ_g	0.146	<i>w</i>	<i>w</i>
F ₂	1 σ_g	0.000	<i>n</i>	
	1 σ_u	0.000	<i>n</i>	
	2 σ_g	0.140	<i>w</i>	
	2 σ_u	0.000	<i>n</i>	
	1 π_u	0.000	<i>n</i>	<i>b</i> (?)
	3 σ_g	0.859	<i>s</i>	
CO	1 π_g	0.000	<i>n</i>	<i>a</i>
	1 σ	0.001	<i>n</i>	
	2 σ	0.001	<i>n</i>	
	3 σ	0.732	<i>s</i>	
	4 σ	0.123	<i>w</i>	<i>w</i>
	1 π	0.829	<i>s</i>	<i>s</i>
CH ₄	5 σ	0.096	<i>n</i> (<i>w</i>)	<i>n</i>
	1 a_1	0.002	<i>n</i>	
	1 t_2	1.020	<i>s</i>	<i>s</i>
	2 a_1	0.990	<i>s</i>	<i>s</i>

* *n* = nonbonding; *a* = antibonding; *b* = moderately bonding; *s* = strongly bonding. Note that v_i cannot distinguish between *a* and *n* since it is always positive.

† For reference to ESCA spectral data and for detailed comments on them see Gopinathan *et al* 1986.

binding energies. Several attempts have been made in the past to formulate a precise theoretical ordinate for these diagrams. Quantities such as MO eigenvalues (Buenker and Peyerimhoff 1974) or their variants (Stenkamp and Davidson 1973) and MO forces (Coulson and Deb 1971) have been tried, but these attempts have only been partially successful. An MO quantity to be successful as the ordinate should have the following properties. It should be a quantitative measure of the bonding power of the MO. Its sum over all occupied MO should yield a molecular quantity that has the extremum value at the equilibrium geometry.

Molecular orbital valency introduced in the previous section satisfies these two requirements. We have seen that MO valency is a quantitative measure of the bonding power of the MO. Further the MO valencies exactly add up to the molecular valency which is a maximum at the equilibrium geometry according to the maximum valency principle. Hence MO valency should serve as the ordinate of Walsh diagrams. This expectation is indeed fulfilled and we have shown that MO valency as the ordinate to produce the Walsh diagrams quite successfully for several molecules (Gopinathan *et al.* 1986; Ravimohan 1984). Figure 3 gives a comparison of the original Walsh diagram and the MO valency diagram for H_2O . In addition to reproducing the qualitative features of the Walsh diagrams, our MO valency diagrams do predict the geometry exactly unlike the original Walsh diagrams. For example, the original Walsh diagram for H_2O predicts a bond angle much less than 90° , whereas the MO valency diagram predicts it as 105° .

A basic assumption in the construction of the original Walsh diagram is that the MO correlation diagrams are the same for a given molecular symmetry species, like AH_2 for instance, and that the features of the diagram are independent of the number of electrons or the state of ionisation of the molecule. We are currently examining the validity of this assumption for the MO valency diagrams.

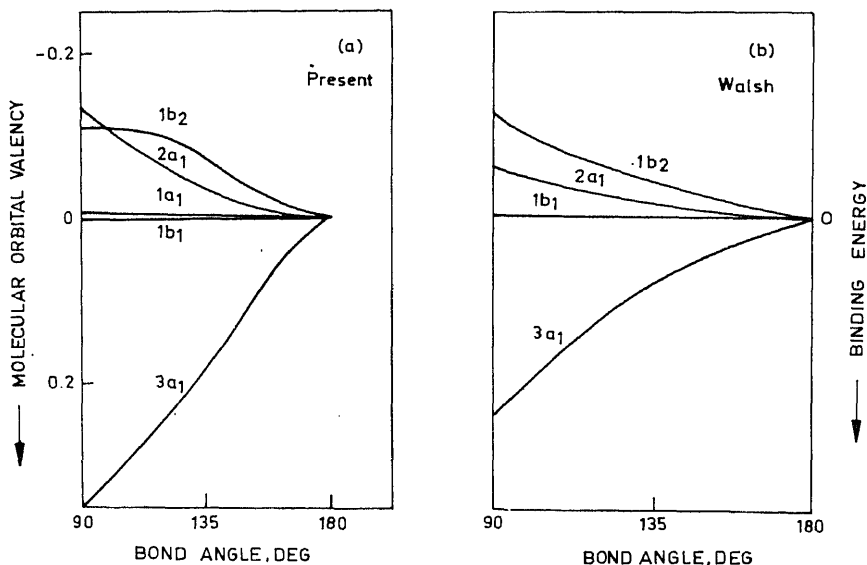


Figure 3. Comparison of the molecular orbital valency diagram (a) for H_2O with the general Walsh diagram, (b) for AH_2 systems.

The valency concept can be used to determine the reactivity of atoms in a molecule to measure the tendency of the atom to form further covalent bonds. The change in valency of atoms in a chemical reaction can be used very convincingly to determine the radical nature of reaction intermediates and transition states and to predict the allowed or forbidden nature of reaction paths. A beginning has been made (Gopinathan and Jug 1983; Jug and Gopinathan 1986) towards such applications of valency and we merely cite some examples here.

As we saw in §2, computed valency values of atoms are scattered around certain integer values like 3 for N, 4 for C etc. We call these values the *normal valencies* and deviations from them as *free valencies*. That is,

$$F_A = V_A^{\text{normal}} - V_A^{\text{actual}}$$

If free valence F_A is positive, the atom is called *subvalent*, and if F_A is negative, the atom is termed *hypervalent*. Notice that the free valence of an isolated atom is equal to its normal valency. The reactivity of atoms in molecules can be rationalised on the basis of the hypothesis (Gopinathan and Jug 1983, p. 511) that atoms tend to reduce their subvalency or hypervalency, and thus revert to their normal valency by making new bonds or by weakening existing ones respectively. For example, O_2 with a subvalency of 25% is highly reactive while N_2 with zero free valency is unreactive. In CO , C is subvalent (36%) and hence reactive, while O with F value of -29% is hypervalent and hence 'antireactive', i.e. it tends to weaken its existing bonds. This is borne out by the tendency of CO to form metal carbonyls by binding through C.

The course of concerted reactions can be predicted by computing the reduction in valency for the transition state. For example (Jug and Gopinathan 1985) for the cyclobutene $\rightarrow$ butadiene reaction, the Woodward-Hoffmann-allowed conrotatory transition state has a reduction of 0.10 in molecular valency whereas the forbidden disrotatory transition state has a reduction of about 2 units of valency. Generally, the path with the minimum reduction in valency is the preferred one. The valency reduction can also be used profitably to determine the radical, biradical or zwitterion nature of transition states and intermediates. The valency method has some advantages (Gopinathan 1985) over other methods for the determination of radical nature of transition states. The method of Salem and Röwland (1972) based on singlet-triplet energy difference and the method of Döhnert and Koutecky (1980) based on natural orbital occupation numbers.

Correlation diagrams of the Woodward-Hoffmann type but employing the molecular orbital valency as the ordinate instead of energy, can be constructed (Siddartha and Jug 1985) to display the allowed and forbidden paths of concerted reactions. For instance, figure 4 shows the variation of the homo valency for the conrotatory and disrotatory cycloaddition of butadiene to cyclobutene. Clearly, for the forbidden disrotatory path there is drastic reduction in homovalency, whereas for the allowed path the molecular valency change is insignificant. Application of this concept to other chemical reactions is under study.

7. Valency and molecular strain

Molecular strain has been attributed to the bent nature of bonds (Coulson and March 1949). Therefore we can expect strain to be related to the reduction in valency.

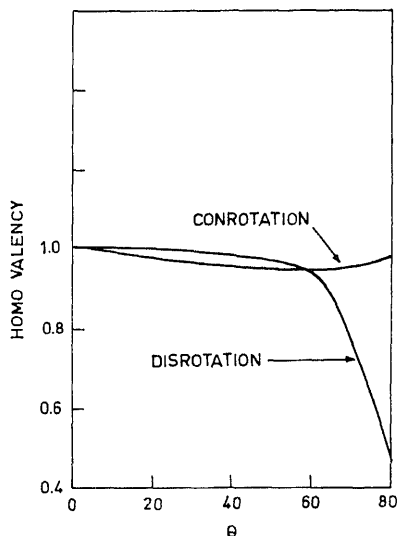


Figure 4. Variation of HOMO valency for the forbidden disrotatory and for the allowed conrotatory cyclisation of butadiene to cyclobutene.

bonds. A bent bond can be considered as consisting of a σ and a π component. The reduction in σ valency in a bent bond compared to that in a strain free bond results in loss of binding energy. This is partly, but not fully, compensated for by the formation of the π component. The net loss in binding energy is the strain energy. We now illustrate this method. The total C–C valency in cyclopropane is 0.99 which can be decomposed into (M S Gopinathan and P Siddarth, unpublished results) a σ valency of 0.83 and a π valency of 0.16. We can view the situation as a loss of 0.17 ($= 1 - 0.83$) σ valency and a gain of 0.16 π valency, compared to a strain free C–C bond of σ valency 1 and π valency 0. Taking the binding energy of a σ C–C bond to be $85 \text{ k cal. mole}^{-1}$ and that of a π C–C bond to be half of the σ bond (since σ and π overlap for carbon p orbitals are roughly in this ratio), we find that the loss in energy is $3 \times (0.17 \times 85 - 0.16 \times 85/2) = 23 \text{ k cal. mole}^{-1}$. This may be compared with the 'experimental' strain energy of $28 \text{ k cal. mole}^{-1}$ for cyclopropane. Inclusion of 'strain' from the C–H bond, which in the present formalism means, a reduction in the valency of the bond compared to that in alkanes, improves the calculated strain close to $28 \text{ k cal mole}^{-1}$.

What is remarkable is that this rather crude approach to strain gives strain energies in surprising agreement with experimental estimates. For example (M S Gopinathan and P Siddarth, unpublished results) we have for cyclobutane 24 (27); cyclopentane 9 (7); cyclopropene 41 (54); cyclobutene 29 (31); cubane 176 (166); here the first quantity is the strain energy estimated from valency and that in paranthesis is the experimental value, all in k cal mole^{-1} .

8. Conclusions

The classical concept of chemical valency can be translated into quantum mechanical language and quantified. This results in a deeper understanding of the fundamental role valency plays in chemical phenomena. We have shown that apart from being a measure of the degree of electron sharing between atoms, which has been its meaning classically, valency determines the shape of molecules through the maximum valency principle; it affords a quantitative measure of the bonding nature of molecular orbitals; it provides the quantitative ordinate for the Walsh diagrams; it can be used: as an index of the chemical reactivity of atoms and of their radical and diradical nature in reactions; to construct correlation diagrams which exhibit the allowed or forbidden nature of reaction paths; and, to estimate the values and to discuss the origin of molecular orbital energies. These various avenues of applications of the valency concept which we have explored remain to be studied in more detail and hopefully new applications await discovery. It is indeed remarkable that the intuitive concept of chemists when quantified and expressed in quantum chemical language can go a long way in our understanding of the structure and behaviour of molecules.

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Direct calculation of energy differences, such as ionization potentials

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Abstract. 'Indirect' methods for the calculation of energy differences imply that two separate calculations of the involved states are performed first and then the difference is taken. In a 'direct' method the transition energy is calculated without an attempt to calculate either of the states between which transition takes place. The theory of direct calculations of energy differences is reviewed with emphasis on ionization potentials and special attention to the method of a common unitary transformation of two model states. Results for the ionization potentials of a few small molecules are presented. The elements of a more general theory are outlined in which the Liouvillean superoperator (and its resolvent) as well as the Fock space formulation of quantum chemistry (especially the concept of effective Hamiltonians in Fock space) play a key role.

Keywords. Energy differences; ionisation potentials; cluster expansion; electron correlation; Liouville operator; Fock space; effective Hamiltonians; Green's function.

1. Introduction

It is not too difficult to calculate the absolute energy of the ground state (or a low-lying excited state) of an atom or a molecule with an error of less than about 1%. Unfortunately, the quantities of physical or chemical interest are not absolute energies, but rather are energy differences, such as binding energies or spectral transition energies. The order of magnitude of these differences is often comparable to the order of magnitude of the errors of the respective absolute energies, such that it is not easy to evaluate these energy differences with sufficient accuracy because one needs to compute the two states in a 'balanced' way.

That this 'indirect' way of the calculation of ionization potentials (IP) can lead to satisfactory results if a sufficiently sophisticated approach is used, has probably been first shown by Meyer (1971, 1973) for the IP of H_2O and CH_4 using the PNO-CI and CEPA-PNO methods.

Methods that lead directly to ionization potentials and transition energies, not as small differences between large numbers, should nevertheless be both more economic and more reliable since contributions to the two states which cancel in the difference need not be evaluated at all.

The simplest approach towards a direct calculation of ionization potentials is due to Koopmans (1933). It is based on two assumptions:

(a) one can describe a molecule in its ground state by a Slater determinant Φ constructed from (doubly occupied) Hartree-Fock orbitals,

(b) the wave function of the ion is obtained by occupying one orbital in the ground state Slater determinant singly rather than doubly, without changing the orbital.

It follows from these two assumptions that the ionization potential I_i is (except for the sign) equal to the Hartree-Fock orbital energy ε_i of the orbital φ_i from which has removed one electron

$$I_i = -\varepsilon_i; F\varphi_i = \varepsilon_i\varphi_i.$$

Koopmans' theorem is often valid to a good degree of approximation, even if the assumptions (a) and (b) are hardly justified. Mulliken (1949) was probably the first to realize that Koopmans' theorem is based to a large extent on a compensation of errors. Koopmans' assumption (b) is certainly wrong; on removal of one electron from the orbital φ_i , the remaining orbitals 'relax', i.e. they adjust to the change in the potential. This relaxation lowers the energy of the ion. The ε_i should hence overestimate the I_i (figure 1).

However, assumption (a) is also not fully correct. Electron correlation lowers the energy as compared to that of a single Slater determinant. This energy lowering is usually larger for a larger number of electrons, i.e. it is larger for the neutral molecule than for the ion. As one sees from figure 1 relaxation and change in correlation energy have usually opposite signs and compensate each other to a large extent.

Mulliken (1949) has also been able to show that Koopmans' theorem is very poor for electron affinities. As one sees from figure 2 the errors due to relaxation and change in the correlation energy have the same sign and do not cancel. The Koopmans value can even have the wrong sign. If one looks at this problem more carefully one also realizes that the energies of unoccupied orbitals are (at variance with those of occupied orbitals) not well defined and basis-dependent such that the Koopmans value for an electron affinity is rather meaningless.

Most more sophisticated direct methods for ionization potentials have in common that they contain Koopmans' approach as the zeroth order step. Direct methods for the calculation of spectral transition energies are closely related. In either case one is interested in the difference of eigenvalues of one Hamiltonian (that has to be interpreted in Fock space for ionization potentials). Unfortunately there is no more promising approach towards a direct calculation of binding energies, because here one has to deal with eigenvalues of different Hamiltonians.

The existing direct methods can be roughly classified as follows

- (a) perturbation-theoretical (Malrieu 1967; Chong *et al* 1974; Kvasnicka and Huzar 1974; Lindgren 1974; Kaldor 1975a, b; Hose and Kaldor 1979)
- (b) non-perturbative (coupled cluster type) (Mukherjee *et al* 1975, 1977; Offerman *et al* 1977)

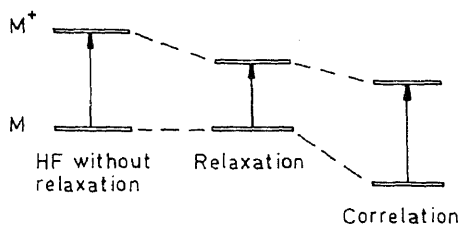


Figure 1. Illustration of Koopmans' theorem for ionization potentials.

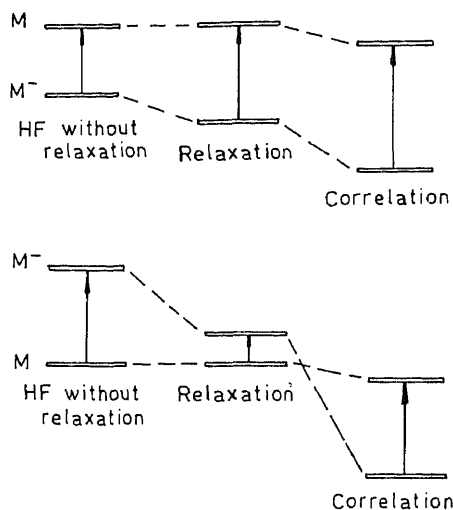


Figure 2. Illustration of Koopmans' theorem for electron affinities.

et al 1976; Monkhurst 1977; Harris 1977; Lindgren 1978; Paldus *et al* 1978; Nakatsuji 1978, 1979; Mukherjee 1979; Mukherjee and Mukherjee 1979; Emrich 1981; Kvasnicka 1981; Jeziorski and Monkhurst 1981; Haque and Mukherjee 1984)

(c) variational or quasi-variational (Westhaus and Bradford 1975; Kutzelnigg 1977; Reitz and Kutzelnigg 1979; Pal *et al* 1984)

(d) based on Green's functions or propagators (Rowe 1968; Dunning and McKoy 1967, 1968; Doll and Reinhardt 1972; Ecker and Holneicher 1972; Cederbaum 1973; Pickup and Goscinski 1973; Simons and Smith 1973; Purvis and Öhrn 1974; Cederbaum and Domcke 1977; Linderberg and Öhrn 1977; Herman *et al* 1977; Oddershede 1978; Öhrn and Born 1981; Schirmer 1982; Schirmer *et al* 1983).

One should note, however, that the Green's function methods also use perturbation theory; non-perturbative Green's function methods have only been proposed recently (Oddershede 1978; Öhrn and Born 1981; Schirmer 1982; Schirmer *et al* 1983). There are further methods that have their origin in simplifications of Green's functions methods, but that can be formulated without referring to Green's functions, such as the RPA (random-phase approximation) or EOM (equations of motions) methods (Rowe 1968; Dunning and McKoy 1967, 1968; Simons and Smith 1973; Herman *et al* 1977; Linderberg and Öhrn 1977).

We do not intend to give a comprehensive review of the subject, we rather concentrate on work of the present authors. Our interest in the direct calculation of energy differences has started with the method of Reitz and Kutzelnigg (1979) that is based on a common unitary transformation of two model states. This method is formally simple and transparent and does not require more effort than perturbation theory to 3rd order—although it is usually quite superior to perturbation theory. It also provides a straightforward analysis of the various corrections to the Koopmans energies. We review this method in §2 and give there also a few results that have so far not been published.

We shall not hide cases where this method is less satisfactory and we shall discuss possible improvements and generalization in §3. This method already contains two ingredients that are essential for a theory of energy differences, namely the central role of a Liouvillean operator and of a Fock space formulation. These concepts will be outlined more generally in §§4, 5 and 7, while §6 is devoted to the concept of effective Hamiltonians in Fock space that allows the most straightforward access to energy differences even in the case of near degeneracies. At the end of §7 the relation of our formalism to that of one-particle Green's functions and propagators in general is briefly mentioned.

2. A common unitary transformation of two model states (Reitz and Kutzelnigg 1979)

Let the neutral ground state be of a closed-shell type such that it can be described to a good degree of approximation by a single Slater determinant 'model wave function' Φ . An approximate wave function Φ' of an excited (or ionized) state can then be constructed from Φ by means of a 'model excitation' (or 'model ionization') operator Ω^+

$$\Phi' = \Omega^+ \Phi, \quad (2)$$

where Ω^+ is a simple annihilation operator a_i for an orbital φ_i occupied in Φ for the case of ionization, or a spin-adapted orbital replacement operator $E_i^{\uparrow}$ in the case of excitation (see §5 for the definition of $E_i^{\uparrow}$).

We search for a unitary wave operator

$$W = e^\sigma, \quad \sigma = -\sigma^+ \quad (3)$$

with the property that it transforms Φ and Φ' simultaneously to the respective exact states Ψ and Ψ'

$$\Psi = e^\sigma \Phi; \quad \Psi' = e^\sigma \Omega^+ \Phi. \quad (4)$$

If we postulate

$$\Omega \Omega^+ \Phi = \Phi, \quad \Omega \Phi = 0 \quad (5)$$

which holds for the model excitation operators mentioned after (2)—we get the following expression for the exact excitation (ionization) energy

$$\begin{aligned} \Delta E &= \langle \Psi' | H | \Psi' \rangle - \langle \Psi | H | \Psi \rangle \\ &= \langle \Phi | \Omega e^{-\sigma} H e^\sigma \Omega^+ | \Phi \rangle - \langle \Phi | \Omega \Omega^+ e^{-\sigma} H e^\sigma | \Phi \rangle \\ &= \langle \Phi | \Omega [e^{-\sigma} H e^\sigma, \Omega^+] | \Phi \rangle = \langle \Phi | [\Omega, [e^{-\sigma} H e^\sigma, \Omega^+]]_{\pm} | \Phi \rangle \\ &= \langle \Phi | [\Omega, [H + [H, \sigma] + \frac{1}{2}[[H, \sigma], \sigma] + \dots], \Omega^+]]_{\pm} | \Phi \rangle, \end{aligned} \quad (6)$$

where it is convenient to choose the $-$ sign (commutator) in $[\dots]_{\pm}$ for (particle-number conserving) excitations and the $+$ sign (anticommutator) for ionization.

There is a stationarity principle (see §4) for energy differences. One can hence determine the optimum wave operator W by requiring that ΔE is stationary with respect

o variations of W (that conserve the unitarity). To exploit this stationarity principle we choose a basis $\{R\}$ of antihermitean operators ($R = -R^\dagger$) and expand σ in this basis

$$\sigma = \sum_R f_R R \quad (7)$$

and determine the optimum f_R by the requirement

$$\frac{\partial \Delta E}{\partial f_R} = 0, \text{ all } R. \quad (8)$$

It is convenient to define the following quantities

$$\begin{aligned} \Delta E_0 &= \langle \Phi | [\Omega, [H, \Omega^\dagger]]_\pm | \Phi \rangle \\ A_R &= \langle \Phi | [\Omega, [[H, R], \Omega^\dagger]]_\pm | \Phi \rangle \\ B_{RS} &= \langle \Phi | [\Omega, [[[H, R], S], \Omega^\dagger]]_\pm | \Phi \rangle \\ C_{RST} &= \langle \Phi | [\Omega, [[[[H, R], S], T], \Omega^\dagger]]_\pm | \Phi \rangle \text{ etc.} \end{aligned} \quad (9)$$

Then (6) becomes

$$\Delta E = \Delta E_0 + \sum_R f_R A_R + \frac{1}{2} \sum_{R,S} f_R f_S B_{RS} + \frac{1}{6} \sum_{R,S,T} f_R f_S f_T C_{RST} + \dots \quad (10)$$

and it results from (8) that

$$A_R + \sum_S f_S B_{RS} + \frac{1}{2} \sum_{S,T} f_S f_T C_{RST} + \dots = 0 \quad (11)$$

$$\Delta E_{\text{opt}} = \Delta E_0 + \frac{1}{2} \sum_R f_R A_R + O(f^3). \quad (12)$$

In principle the system (11, 12) is exact. In practice one can get only an approximation to the exact ΔE , because (a) one can never choose a complete operator basis $\{R\}$, (b) the Hausdorff expansion in (10) or (11) is infinite and one must truncate it after some commutator rank.

The simplest non-trivial approximation consists in (1) limiting $\{R\}$ to a basis of one-particle and two-particle operators (φ_i and φ_j are supposed to be occupied in Φ , φ_p and φ_q arbitrary)

$$R = \begin{cases} a_p^\dagger a_i - a_i^\dagger a_p \\ a_q^\dagger a_p^\dagger a_j a_i - a_i^\dagger a_j^\dagger a_p a_q \end{cases} \quad (13)$$

or rather spin adapted linear combinations of such operators.

(2) truncating (10) after the bilinear terms. This makes the system (11) linear

$$A_R + \sum_S f_S B_{RS} = 0; \quad \Delta E = \Delta E_0 + \frac{1}{2} \sum_R f_R A_R \quad (14)$$

This linear approach for energy differences is analogous to the CEPA-0 (linear CP-MET or linearized coupled-cluster) approach for the correlation energy of single closed shell states. It is, *grosso modo* (see §3) equivalent to perturbation theory up to third order with infinite summation of all ladder diagrams. The computational effort is

not larger than for perturbation theory to third order, since the same matrix elements have to be evaluated in either case.

The matrix elements (9) involve only commutators of operators. This Lie-algebra structure implies that in a diagrammatic formulation only 'connected' diagrams contribute. Only such R or S contribute to A_R or B_{RS} , which have at least one pair or hole index in common with Ω^+ . In the case of ionization from the orbital φ_i , only operators represented graphically on figure 3 contribute in the linear theory. Operators can easily be classified as those that account for: (a) relaxation; (b) polarization; (c) change of external correlation; (d) semi-internal correlation.

The terms internal, semiinternal and external correlation have been defined by Silverstone and Sinanoglu (Sinanoglu 1964; Silverstone and Sinanoglu 1966) in a fundamental paper on electron correlation in open-shell states.

In the zeroth-order approximation where ΔE is given by ΔE_0 one gets just the Koopmans energy, i.e. ΔE_0 is equal to the Hartree-Fock energy of the orbital that 'ionizes off'. In performing separate restricted Hartree-Fock calculations for the neutral ground state Φ and the ion Φ' and taking the difference one accounts in addition to ΔE_0 for relaxation. In order to take care of spin-polarization as well, at least unrestricted (better spin-projected unrestricted) Hartree-Fock calculations are necessary.

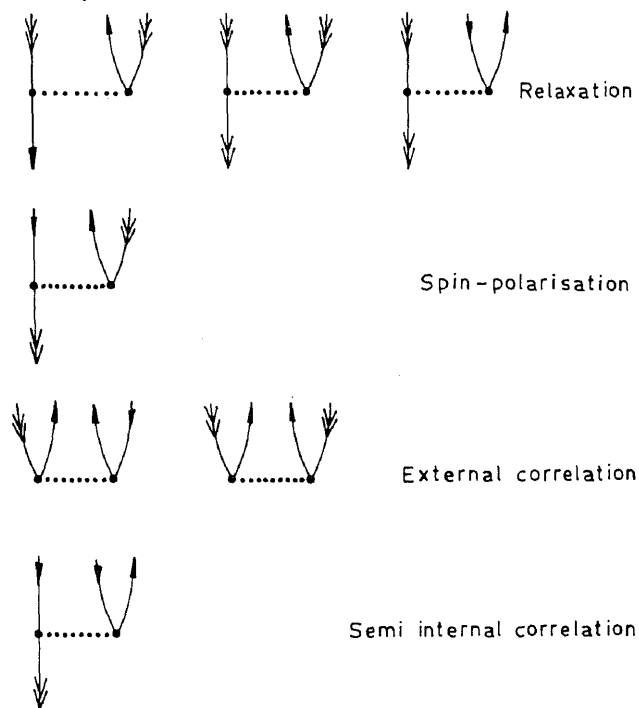


Figure 3. Lowest order contributions to the wave operator for ionization.

Some results are collected in the tables 1 to 4. The general conclusions are:

(a) Except for some special cases [to be discussed under (d)] the results agree well with experiment if the basis sets are large enough.

(b) For ionization from the valence shells, Mulliken's interpretation is confirmed, according to which the approximate validity of Koopmans' theorem is based on a large cancellation of relaxation and change in correlation energy (see tables 1 and 2).

(c) For ionization from inner shells the contribution of relaxation is very strong, while there is only a minor change in correlation energy (Meyer 1971, 1973; Reitz and Kutzelnigg 1979) Koopmans' theorem is hence not a very good approximation. One gets then a much better ionization potential from separate SCF calculations of the

Table 1. Ionization potentials for neon (in a.u.), basis: 9s5p2d1f.

	2p	2s
Koopmans-IP	0.84465	1.92392
Relaxation	-0.10687	-0.10668
Spin-polarization	-0.01081	-0.00942
External double substitutions	0.08147	0.04858
Semiinternal double substitutions	-0.01432	-0.07396
Result	0.79413	1.78245
Experiment*	0.7938	1.7813

* C E Moore 1949 Atomic Energy Levels, Natl. Bur. Stand. (U.S.) Circular 467, Vol. I.

Table 2. Ionization potentials for CH₄ (in a.u.), basis 951/51.

	1t ₂	2a ₁
Koopmans	0.54430	0.94206
Relaxation	-0.04102	-0.05153
Spin-polarization	-0.00985	-0.00813
External double substitution	0.05556	0.03970
Semiinternal double substitution	-0.01864	-0.08422
Result	0.53036	0.83798
Experiment	0.52920	0.84157

Table 3. Ionization potentials for argon (in a.u.), basis 1172.

	3p	3s
Koopmans IP	0.58395	1.27144
Relaxation	-0.04002	-0.05647
Spin-polarization	-0.01092	-0.00662
External double substitution	-0.05730	0.02749
Semiinternal double substitution	-0.01525	-0.28498
Result	0.57507	0.95085
Experiment	0.57920	1.07457

Table 4. Vertical valence shell ionization potentials in eV.

Compound	Ionization potentials			Basis
<u>CH₄</u>				
UNITR*	14.43	22.80		951/51
Experimental	14.40	22.90		
<u>NH₃</u>				
UNITR	10.81	16.63		951/51
Experimental	10.9	15.8 to 16.5		
<u>H₂O</u>				
UNITR	12.72	14.95	19.09	951/51
Experimental	12.78	14.83	18.72	
<u>HF</u>				
UNITR	16.30	20.12		9521/51
UNITR	16.00	19.99		951/51
Experimental	16.04	19.90		
<u>Ne</u>				
UNITR	21.61	48.50		9521
Experimental	21.60	48.47		
<u>H₂S</u>				
UNITR	10.25	13.33		1172/51
Experimental	10.47	13.33		
<u>HCl</u>				
UNITR	12.39	16.50		1171/51
UNITR	12.55	16.58		1172/51
Experimental	12.8	16.6		
<u>Ar</u>				
UNITR	15.65	25.87		1172
Experimental	15.76	29.24		
<u>Cl⁻</u>				
UNITR	3.68	10.46		1172
Experimental	3.61	?		
<u>N₂</u>				
UNITR	15.02	17.37		952
Experimental	15.60	16.98		

* the method outlined in §2.

neutral molecule and the ion. This case is not documented here.

(d) In some cases the agreement with experiment is not satisfactory, e.g. for the ionization of a 3s-AO from Ar (see table 3). Here the 'semiinternal' contribution to the IP is unusually large. This is an indication of near-degeneracy of the ionized configuration $1s^2 2s^2 2p^6 3s 3p^6$ with the 'semiinternally' excited ionic configuration $1s^2 2s^2 2p^6 3s^2 3p^4 3d$ (it is, with respect to the former configuration, doubly excited $3p^2 \rightarrow 3s 3d$, $3p \rightarrow 3s$ is 'internal', $3p \rightarrow 3d$ 'external').

Another case of poor agreement between theory and experiment is the ionization potential of F^- (equivalent to the electron affinity of F). Here one finds an unusually large relaxation contribution. If one particular contribution is very large, one can conclude that the lowest order approach (14) is not good enough.

The following remark is in order. Many ionic states are not really bound states, especially those where an electron is ionized from an inner orbital. There is no guarantee that variational calculations converge to such states. The corresponding

Koopmans states are, however, well defined. It also seems that 'direct' methods with the Koopmans energy as starting approximation have no convergence problems.

3. Possible improvement of the method of §2

The method proposed by Reitz and Kutzelnigg (1979) leads to rather simple expressions, and does not, in fact, involve more labour than perturbation theory up to 3rd order. It is not entirely true that this method contains all contributions of 3rd order of PT. In truncating the energy expansion (10) after the bilinear terms one neglects the contribution

$$\frac{1}{3!} \langle \Phi | [\Omega, [[[[H_0, \sigma], \sigma], \sigma], \Omega^+]] + |\Phi \rangle, \quad (15)$$

the leading term of which is of $O(\lambda^3)$. It is not too difficult to define an alternative hierarchy of truncation, in which one includes terms with H_0 to one order higher in the Hausdorff expansion than terms with V . It appears, however, that terms like (15) are relatively unimportant.

If one goes to higher orders in the Hausdorff expansion (10) one is led to non-linear systems of equations and the matrix elements become rather complicated. This does not really pay, unless one also increases the particle rank of the basis operators. One can again argue in terms of perturbation theory. To 3rd order in PT only two-particle operators contribute, while one needs three-particle operators to get all terms of 4th and 5th order in PT. So the next consistent step in a hierarchy of equations would be to

- (a) truncate the basis after three-particle operators
- (b) truncate the Hausdorff expansion after the term

$$\frac{1}{4!} \langle \Phi | [\Omega, [[[[[H, \sigma], \sigma], \sigma], \sigma], \Omega^+]] + |\Phi \rangle \quad (16)$$

or

$$\frac{1}{4!} \langle \Phi | [\Omega, [[[[[V, \sigma], \sigma], \sigma], \sigma], \Omega^+]] + |\Phi \rangle \quad (17a)$$

and

$$\frac{1}{5!} \langle \Phi | [\Omega, [[[[[[H_0, \sigma], \sigma], \sigma], \sigma], \sigma], \Omega^+]] + |\Phi \rangle. \quad (17b)$$

One can also argue that 3-particle operators are $O(\lambda^2)$ such that one can reduce the maximum order in the Hausdorff expansion by one for each 3-particle operator.

Although one can thus define a hierarchy that leads eventually to the exact result, this may not be the optimum way. As in the theory of electron correlation of single electronic states, it is recommended that a distinction be made between so-called dynamic and non-dynamic correlation effects (Sinanoglu 1964). In the language of perturbation theory, dynamic correlation effects (which come mainly from the short range Coulomb repulsion) are associated with large energy denominators ε and hence, small coefficients c

$$c = A/\varepsilon; \quad \Delta E = A^2/\varepsilon = Ac. \quad (18)$$

Non-dynamic correlation effects result from near degeneracies and are associated with small ε (in absolute value) and hence, large coefficients c . Perturbation theory converges

perturbation theory or the non-perturbative analogues of these theories.

In practice this means that one does not consider a single reference state but a manifold of quasidegenerate states together, as in the theory of effective Hamiltonians presented in §6. In the theory of energy differences the analogue would be to consider a manifold of quasidegenerate reference energy differences together. In the case of the ionization potentials of Ar, the states $1s^2 2s^2 2p^6 3s 3p^6$ and $1s^2 2s^2 2p^6 3s^2 3p^4 3d$ should be considered together. This is certainly more effective than to go to the next step of the hierarchy using brute force.

4. Superoperator theory

A general theory of energy differences (more precisely: of differences of the eigenvalues of one Hamiltonian) can be based on the superoperator (Liouvillean) formalism (Goscinski and Lukman 1970; Jörgensen 1975; Dalgaard and Simons 1977; Manne 1979; Dalgaard 1979; Weiner and Goscinski 1980; Oddershede 1982; Prasad *et al* 1985). Let $\hat{H}$ be a Hamiltonian, then we define the corresponding superoperator $\mathbf{H}$ as

$$\mathbf{H}\hat{X} = [\hat{H}, \hat{X}] = \hat{H}\hat{X} - \hat{X}\hat{H} \quad (19)$$

for arbitrary $\hat{X}$. H acts on operators (while $\hat{H}$ acts on functions). Let

$$\hat{H}\Psi_\mu = E\Psi_\mu; \quad \hat{P}_{\mu\nu} = |\Psi_\mu\rangle\langle\Psi_\nu|, \quad (20)$$

then

$$\mathbf{H}\hat{P}_{\mu\nu} = (E_\mu - E_\nu)\hat{P}_{\mu\nu} = \omega_{\mu\nu}\hat{P}_{\mu\nu}, \quad (21)$$

i.e. the 'excitation operators' (shift operators) $\hat{P}_{\mu\nu}$ are eigenoperators of $\mathbf{H}$ to the eigenvalues $\omega_{\mu\nu} = E_\mu - E_\nu$.

If one introduces a scalar product and matrix elements in operator space

$$\langle\hat{A}|\hat{B}\rangle = \text{Tr}\{\hat{A}^+\hat{B}\}; \quad \langle\hat{A}|\mathbf{H}|\hat{B}\rangle = \text{Tr}(\hat{A}^+(\mathbf{H}\hat{B})) \quad (22)$$

a stationarity principle for energy differences can be formulated

$$\delta\{\langle\hat{X}|\mathbf{H}|\hat{X}\rangle - \lambda\langle\hat{X}|\hat{X}\rangle\} = 0 \quad (23)$$

One can then expand $\hat{X}$ in an operator basis, evaluate the matrix elements of H in this operator basis and get the transition energies ω as well as the corresponding excitation operators $\hat{P}$ from a matrix eigenvalue problem. Note, however, that (23) is only a stationarity—not an extremum—principle. By making (23) stationary one does hence get neither upper nor lower bounds to the respective energy differences. One is only sure that the error of ω is quadratic in the error of $\hat{P}$.

Usually this expansion method does not present any advantage as compared to the corresponding expansion method for the original Schrödinger equation (20) because an operator basis is always larger than a function basis. The superoperator formalism only becomes competitive if one applies it in Fock space (with the particle number not fixed) rather than in a fixed-particle number Hilbert space. In fact superoperator theory can be applied to ionization only if one interprets $\hat{H}$ as a Fock space operator. The main advantage of Fock space theory is that the operator basis is much simpler than in fixed particle number Hilbert space (see §7).

The formalism (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983) outlined in this section is essentially equivalent to traditional 2nd quantization, it mainly uses a more compact notation, in particular for particle-number conserving normal products of creation ($a_p^+ = a^p$) and annihilation operators (a_p)—that are defined with respect to an orthonormal one-particle (spin-orbital) basis Ψ_p . We define

$$\begin{aligned} a_q^p &= a^p a_q = a_p^+ a_q \\ a_{rs}^{pq} &= a^p a^q a_s a_r, \quad \text{etc.} \end{aligned} \quad (24)$$

as well as the corresponding operators summed over spin (which are hence spin-independent, i.e. spin-conserving)

$$\begin{aligned} E_Q^P &= a_{Q\alpha}^{P\alpha} + a_{Q\beta}^{P\beta} \\ E_{RS}^{PQ} &= a_{R\alpha S\alpha}^{P\alpha Q\alpha} + a_{R\alpha S\beta}^{P\alpha Q\beta} + a_{R\beta S\alpha}^{P\beta Q\alpha} + a_{R\beta S\beta}^{P\beta Q\beta} \quad \text{etc.} \end{aligned} \quad (25)$$

Capital letters always refer to spinfree orbitals, lower case are letters to spin orbitals.

A tensorial notation is also used for matrix elements (bras: lower indices, kets: upper indices)

$$\begin{aligned} \langle \varphi_P | h | \varphi_Q \rangle &= h_P^Q \\ \langle \varphi_P(1) \varphi_Q(2) | \frac{1}{r_{12}} | \varphi_R(1) \varphi_S(2) \rangle &= V_{PQ}^{RS} \end{aligned} \quad (26)$$

A spinfree Hamiltonian looks then like

$$H = h_P^P E_P^Q + \frac{1}{2} V_{RS}^{PQ} E_{PQ}^{RS} \quad (27)$$

where the Einstein summation convention is implied.

In practice one has to use a *finite* basis $\{\varphi_R\}$ of M (spinfree) orbitals. The H according to (27) in such a finite basis is invariant under the unitary group $U(M)$ of all unitarity transformations among the M basis functions. As a consequence the eigenfunctions of H must transform as irreducible representations (ir) of $U(M)$. These ir are labelled by the particle number N , the particle statistics (fermions, bosons, spinfree electrons), and the total spin. Basis vectors corresponding to these ir have been derived by Gelfand and Setline (1950), and these have become very popular in quantum chemistry (Hinze 1981). It is also possible to label the ir by Young diagrams (for electrons with maximally two columns) and the basis vectors by Young tableaux.

All important invariants (except those related to point group symmetry) appear as labels of the ir of $U(M)$.

One should keep in mind that the unitary group $U(M)$ plays the same natural role in rock space theory as the symmetric group $S(N)$ plays in configuration space theory. These two groups have common ir.

The Fock space analogue to the solution of the Schrödinger equation is the search for similarity transformation of H to a 'diagonal' operator L

$$L = W^{-1} H W; \quad L = L_D \quad (28)$$

where W means of an operator W . To make this transformation meaningful one must first define what one understands by 'diagonal'. There are various possibilities (Kutzelnigg

1981, 1982, 1984a, b, Kutzelnigg and Koch 1985), two of which are especially important. In either case one first chooses a one-electron operator H_0 and chooses the orbital basis as eigenfunctions of H_0

$$H_0 = e_p E_p' \quad (29)$$

Let B be an arbitrary Fock space operator

$$B = B_0 + B_Q^p E_Q^p + \frac{1}{2} B_{RS}^{PQ} E_{PQ}^{RS} + \dots \quad (30)$$

In the sense of the first definition (universal theory) the 'diagonal part' B_D of B is defined as

$$B_D = B_0 + \delta(e_p, e_Q) B_Q^p E_Q^p + \delta(e_p + e_Q, e_R + e_S) B_{RS}^{PQ} E_{PQ}^{RS} + \dots \quad (31)$$

with $\delta(x, y)$ a Kronecker delta. The second definition (theory of effective Hamiltonians) is based on a division of the one-particle space into an 'active' subspace (indices $X, Y, Z \dots$) and an 'inactive' subspace (indices $A, B, C \dots$). Operators can then be divided into four classes.

B : closed from below, e.g. E_{XY}^{AB}, E_{XY}^{AX}

A : closed from above, e.g. E_{AB}^{XY}, E_{AX}^{XY}

C : closed e.g. E_Y^X, E_{ZX}^{XY}

O : open e.g. E_{AB}^{CD}, E_{AX}^{BY} , etc. (32)

The diagonal part of an operator is then defined as

$$B_D = B_C + B_0. \quad (33)$$

For either definition (31) or (33) the 'nondiagonal' part B_N is the complement

$$B_N = B - B_D \quad (34)$$

An operator is called 'diagonal' if it is equal to its diagonal part.

We rewrite (28) as

$$HW = WL; \quad L = L_D, \quad (35)$$

and decompose both H and L as

$$H = H_0 + \lambda V; \quad L = H_0 + \Delta L, \quad (36)$$

with H_0 given by (29). If H_0 is the bare nuclear Hamiltonian, then

$$V = \frac{1}{2} V_{RS}^{PQ} E_{PQ}^{RS}. \quad (37)$$

From (35) and (36) we get

$$[H_0, W] = -\lambda VW + W\Delta L. \quad (38)$$

We use the following short hand notation for the formal solution of a commutator equation

$$[H_0, X] = Y \Rightarrow X = -Y_H, \quad (39)$$

where one has to keep in mind that this solution only exists if $Y_D = 0$, and that even then the solution X is not unique, since one can always add to X any operator Z which

$$B_H = (e_P - e_Q)^{-1} (B_Q^P E_P^Q)_N + (e_P + e_Q - e_R - e_S)^{-1} (B_R^P E_P^Q)_N + \dots \quad (40)$$

Equation (38) can either be solved by perturbation theory (i.e. expanding W and ΔL in powers of λ and collecting the same powers of λ) or iteratively (where some convergence acceleration is recommended). Details are found elsewhere (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983).

Equations (35) or (38) do not determine W and L uniquely. To make W and L unique one has to impose a so-called 'normalization condition'. There are many different possibilities with different merits and drawbacks. The most important ones are the following.

$$\begin{aligned} W_D = 1: & \text{intermediate normalization,} \\ WW^+ = 1; W_D = W_D^+: & \text{canonical unitary normalization,} \\ WW^+ = 1; (\ln W)_D = 0: & \text{separable unitary normalization.} \end{aligned} \quad (41)$$

The third possibility is most conveniently formulated in terms of an operator σ

$$W = e^\sigma; \quad \sigma = -\sigma^+ = \sigma_N. \quad (42)$$

The intermediate normalization leads to simpler expressions, but to a non-hermitean L . If one wants a hermitean L one must choose W unitary.

It is finally convenient to introduce a particle-hole formalism (Kutzelnigg 1984a, b), in such a way that normal products of operators are understood in a particle-hole sense but that upper labels are never changed to lower labels and vice versa. If we label holes as $I, J, K \dots$ and particles as A, B, C the (particle number and spin conserving) operators are

$$\begin{aligned} \tilde{E}_J^I &= -2\delta_J^I + E_J^I \\ \tilde{E}_B^A &= E_B^A; \tilde{E}_A^I = E_A^I; \tilde{E}_I^A = E_I^A \end{aligned} \quad (43)$$

and respective expressions for operators of higher particle rank. Operators in particle-hole sense are represented by a tilde as $\tilde{E}_J^I$.

In evaluating (38) one has to build products of Fock space operators. This can be done by means of a generalized Wick theorem (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983), e.g.

$$\tilde{E}_{CD}^{AB} \tilde{E}_F^E = \tilde{E}_{CDQ}^{ABE} + \delta_C^E \tilde{E}_{FD}^{AB} + \delta_D^E \tilde{E}_{CF}^{AB} \quad (44)$$

Particle indices 'contract' from upper right to lower left, hole lines from lower right to upper left. Contraction over hole lines introduces a factor -1 , 'closed loops' yield a factor (-2) .

Effective Hamiltonians and energy differences

Let us choose the definition of B_D which corresponds to partitioning the one-particle space into 'active' and 'inactive' subspaces and let us also choose the particle-hole formalism which amounts to discriminating between 'particle' and 'hole' states. This means we can have as many as 4 classes of one-particle states.

(a) active hole states: labels $F, G \dots$,

- (b) inactive hole states: labels $I, J, K \dots$,
- (c) active particle states: labels $X, Y, Z \dots$,
- (d) inactive particle states: labels A, B, C .

We illustrate this for two examples. Let us first assume that we want to describe the Mg atom both in its neutral ground state (configuration $1s^2 2s^2 2p^6 3s^2$) and in the ground state of the Mg^+ ion ($1s^2 2s^2 2p^6 3s$). We start with an SCF calculation of the Mg^{2+} core ($1s^2 2s^2 2p^6$) and define the AO $1s, 2s, 2p$, that are occupied in the core, as inactive hole states. The valence AO $3s$ will be regarded as an active particle state and all other (virtual) AO as inactive particle states (in this example there are no active hole states).

The effective Hamiltonian is then (it only acts on active orbitals)

$$L = \tilde{L}_\nu + \tilde{L}_X^X \tilde{E}_X^X + \frac{1}{2} \tilde{L}_{XX}^{XX} \tilde{E}_{XX}^{XX}, \quad (45)$$

where $\tilde{L}_\nu$ is the energy of the 'physical vacuum' (i.e. the Mg^{2+} core) and where X means the $3s$ -AO. One sees easily that

$$\begin{aligned} E(Mg^+, 3s) &= \tilde{L}_\nu + \tilde{L}_X^X, \\ E(Mg, 3s^2) &= \tilde{L}_\nu + 2\tilde{L}_X^X + \tilde{L}_{XX}^{XX}, \\ IP = E(Mg) - E(Mg^+) &= \tilde{L}_X^X + \tilde{L}_{XX}^{XX}. \end{aligned} \quad (46)$$

For this particular example we calculate (Koch 1984)

$$\begin{aligned} \tilde{L}_X^X &= -14.945 \text{ eV}, \\ \tilde{L}_{XX}^{XX} &= 7.324 \text{ eV}, \\ IP &= 7.621 \text{ eV (experimental 7.646 eV)}. \end{aligned}$$

The ionization potential (IP) of neutral magnesium is hence easily expressed through the matrix elements of the effective Hamiltonian (45).

An alternative would be to take the ground state of neutral Mg ($1s^2 2s^2 2p^6 3s^2$) as 'physical vacuum' and to start with an SCF calculation of this state. We have then to classify $1s, 2s$ and $2p$ as inactive hole states and $3s$ as an active hole state; all other (virtual) AO are inactive particle states.

The effective Hamiltonian is then

$$L = \tilde{L}_\nu + \tilde{L}_F^F \tilde{E}_F^F + \frac{1}{2} \tilde{L}_{FF}^{FF} \tilde{E}_{FF}^{FF}, \quad (47)$$

where $\tilde{L}_\nu$ is now the energy of the Mg ground state. The IP of Mg (for ionization for the $3s$ -AO) is then directly $-\tilde{L}_F^F$.

It is not easy to say *a priori* which of the two choices is better. One may, in view of the $3s/3p$ near-degeneracy also want to consider the $3p$ -AO as active particles, which makes the effective Hamiltonian more complicated, but may make the constructions of its elements easier.

For the case of the '3s-IP' of Ar we have to regard $1s, 2s$ and $2p$ as inactive hole states, $3s$ and $3p$ as active hole states and $3d$ as active particle states—or alternatively $3s, 3p$ and $3d$ as active particle states. In either case the IP is not directly expressible through the matrix elements of the effective Hamiltonian, but a secular problem in the active space

1958; Morita 1963; Brandow 1967; Kirtman 1968; Amat *et al* 1971; Schücan and Weidenmüller 1973; Klein 1974; Lindgren 1974; Jørgensen 1975; Kvasnicka 1977; Barret 1977; Shavitt and Redmon 1980; Soliverez 1981; Sun *et al* 1981; Powers and Zuker 1981; Durand 1983).

7. The Fock space Liouville operator

Let $\hat{H}$ be a Fock space Hamiltonian as given by (27). We define (in analogy to §4) the Fock space Liouvillean $\mathbf{H}$ via

$$\mathbf{H}\hat{Y} = [\hat{H}, \hat{Y}]. \quad (48)$$

The eigenstates of $\mathbf{H}$ according to

$$\mathbf{H}\hat{X} = \omega\hat{X} \quad (49)$$

are now transitions between eigenstates of $\hat{H}$ either for the same or different numbers of particles. In analogy to the particle number operator $\hat{N}$ there is the superoperator $\mathbf{N}$ of the change of the number of particles

$$\mathbf{N}\hat{Y} = [\hat{N}, \hat{Y}]. \quad (50)$$

The eigenoperators of $\mathbf{H}$ are, of course, also eigenoperators of $\mathbf{N}$. Let $\hat{H}_0$ be a one-particle operator

$$\hat{H}_0 = e_p E_p^p, \quad (51)$$

then every E_S^R is eigenoperator of $\mathbf{H}_0$ to the eigenvalue $(e_R - e_S)$ and of $\mathbf{N}$ to the eigenvalue 0 (no change in the number of particles). The following operators

$$E_{SP}^{RP}, E_{PS}^{RP}, E_{SPQ}^{RPQ}, \text{ etc.} \quad (52)$$

are also eigenoperators of $\mathbf{H}_0$ and $\mathbf{N}$ to the same eigenvalues. Any eigenvalue of $\mathbf{H}_0$ is hence highly degenerate (E_S^R means 'unconditional' excitation from φ_S to φ_R , while E_{SP}^{RP} means excitation from φ_S to φ_R provided that φ_P is occupied etc.). This degeneracy is to a large extent removed by the interaction superoperator $\mathbf{V}$. It is obvious that degenerate or quasidegenerate perturbation theory has to be applied, unless one succeeds in removing this degeneracy by referring to super operators that commute with $\mathbf{H}$.

If one performs perturbation theory for energy differences with the Fock space Liouvillean formalism one gets the same results as from perturbation theory of the two states separately and forming the difference. However, due to the Lie algebraic structure of the theory, contributions that are not connected to the excitation (or ionization) and that cancel in the difference do not appear at the outset. This leads to a simplification.

The generalization of the Frobenius trace metric to Fock space operators is non-trivial but possible (Kutzelnigg 1986).

A non-perturbative approach to ionization potentials leads to the Reitz-Kutzelnigg method of §2 as the simplest non-trivial approximation. For excitation energies one is easily lead to RPA (random phase approximation) as a possible first step in a hierarchy of approximations. Alternative hierarchies have been proposed by Schirmer *et al* (1983).

As for any operator or superoperator the resolvent $\mathbf{G}(z)$ of the Fockspace Liouvillean $\mathbf{H}$ can be defined via

$$\mathbf{G}(z)(z - \mathbf{H}) = \mathbf{1}, \quad (53)$$

which means explicitly

$$\mathbf{G}(z)(z\hat{Y} - [\hat{H}, \hat{Y}]) = \hat{Y} \quad (54)$$

for all $\hat{Y}$ in the domain of $\mathbf{H}$. One also writes formally

$$\mathbf{G}(z) = (z - \mathbf{H})^{-1}. \quad (55)$$

We also define the unperturbed resolvent $\mathbf{G}_0$, related to the $\hat{H}_0$ given by (51)

$$\mathbf{G}_0(z) = (z - \mathbf{H}_0)^{-1}. \quad (56)$$

All normal products of an arbitrary number of creation and annihilation operators for the eigenstates of $\hat{H}_0$ are eigenoperators of $\mathbf{G}_0(z)$, e.g.

$$\begin{aligned} \mathbf{G}_0(z)a_p &= (z + e_p)^{-1}a_p \\ \mathbf{G}_0(z)a^q &= (z - e_q)^{-1}a^q \\ \mathbf{G}_0(z)a_{rs}^{pq} &= (z - e_p - e_q + e_r + e_s)^{-1}a_{rs}^{pq} \end{aligned} \quad (57)$$

The well-known relation between $\mathbf{G}(z)$, $\mathbf{G}_0(z)$ and $\mathbf{V}$ also holds in this case*

$$\mathbf{G}(z) = \mathbf{G}_0(z) + \mathbf{G}_0(z)\mathbf{V}\mathbf{G}(z). \quad (58)$$

The resolvent $\mathbf{G}(z)$ has poles for all those values of z that are equal to the eigenvalues of $\mathbf{H}$ i.e. to differences of eigenvalues of $\hat{H}$. This is usually too much information. One wants to filter it to transitions from a given state $\bar{\Psi}$ to, say all the states in which the particle number is reduced by 1—i.e. to ionization. This can be achieved by considering the expectation value

$$\langle \Psi | [\Omega, \{\mathbf{G}(z)\Omega^+\}]_+ | \Psi \rangle, \quad (59)$$

where

$$\Omega^+ = a_i, \quad (60)$$

is a model ionization operator and Ψ the exact wave function of the ground state. From (59) there is a straightforward way to the theory of Green's functions for reduced particle number or of propagators and to a time-independent theory of these Green's functions (Kutzelnigg 1986) which are conventionally introduced and evaluated in a time-dependent formulation (see for example, Kirshnitz 1967; Fetter and Walecka 1971; Parry 1973), and which have largely been used for the direct calculation of energies by various authors, primarily by Cederbaum and his group (Cederbaum 1973; Cederbaum and Domcke 1977). Time-independent approaches to Greens functions have also been considered by other authors (Goscinski and Lukman 1970; Jørgensen 1975; Dalgaard and Simons 1977; Dalgaard 1979; Manne 1979; Weiner and Goscinski 1980; Oddershede 1982; Prasad et al 1985).

* This is sometimes called a 'Lippman-Schwinger' equation, although the latter refers to a different physical situation viz the inclusion of scattering boundary conditions.

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Dynamics of bond-formation in some bound states of HeH^+

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Abstract. The role of the electronic kinetic energy and its Cartesian components is examined during the formation of the ground ($^1\Sigma$), the first excited ($^1\Sigma$)* and the lowest ($^3\Sigma$) states of HeH^+ employing wavefunctions of the multi-configuration type with basis orbitals in elliptic coordinates. Results show, contrary to earlier beliefs, that the bond formation in these states is preceded primarily by a charge transfer from the neutral atom to the ion. There is no evidence of polarisation of the neutral atom orbitals by the ion even at large internuclear separation.

Keywords. Kinetic energy; bond-parallel and bond-perpendicular components; interference effect; charge transfer.

1. Introduction

The singly charged helium hydride molecular ion is known for many years from mass spectroscopic studies (Hogness and Lunn 1925). The ground state, ($^1\Sigma$), of HeH^+ dissociates into $\text{He} + \text{H}^+$ and is quite stable. The first excited ($^1\Sigma$)* and the lowest ($^3\Sigma$) states of HeH^+ dissociate into $\text{He}^+(^2S) (1s)$ and $\text{H}(^2S) (1s)$ with an exact energy of -2.5 Hartree. A good deal of discussion as to the nature of the first excited state of HeH^+ has appeared mainly because the exact shape of the potential curve is important in analysing the β -decay of the HT molecule as reported by Snell (1957) and Wexler (1959). These two excited states of HeH^+ are weakly bonding with an equilibrium separation of 5.5 Bohr for the first excited ($^1\Sigma$)* state and 4.5 Bohr for the lowest ($^3\Sigma$) state. Chemical bonding in these systems have been studied earlier by various authors (Coulson and Duncanson 1938; Hurley 1956; Anex 1963; Stuart and Matsen 1964; Peyerimhoff 1965; Politzer 1966; Michels 1966; Butscher and Schmidtke 1978). Classically the interaction between a polarisable atom and a singly charged particle produces an induced dipole in the atom and the energy change is given by

$$\Delta E = -\alpha/2R^4, \quad (1)$$

where α is the polarisability of the neutral atom and R is the internuclear separation. It had been shown by many authors (Stuart and Matsen 1964; Politzer 1966) that the polarisation interaction energies are quite close to the binding energies although an increasing discrepancy arises at small R values. The formation of the ground state ($^1\Sigma$) of HeH^+ was therefore viewed as resulting from polarisation of the He atom by H^+ , and that the exchange or interference effect was not important. Similarly the formation of the first excited ($^1\Sigma$)* and the lowest ($^3\Sigma$) states of HeH^+ was thought to arise from polarisation of the H-orbital by He^+ (Michels 1966). A previous study (Chandra and

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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Sebastian 1976) on bond formation in terms of electronic forces also reveal that origin of bonding in these two excited states is the ion-induced dipole type interaction. However, our recent study (Rama Rao and Chandra 1985) of the formation process in terms of the bond-parallel and bond-perpendicular components of kinetic energy show that polarisation is not important in the excited states.

In this paper we consider simple configuration interaction wavefunctions using orbitals in elliptic coordinates and then study the behaviour of the total electronic kinetic energy and its cartesian components as a function of R to reveal the dynamics of the bond-formation process in the ground, $(^1\Sigma)$ and excited $[(^1\Sigma)^*, (^3\Sigma)]$ states of HeH^+ . We then correlate our results derived from the kinetic energy to the changes in electron densities that occurs during the formation process.

2. Computation of wavefunctions

We have chosen a simple configuration interaction wavefunction of the form

$$\Psi = \sum_i C_i \psi_i(\hat{r}),$$

where the spatial part $\psi_i(\hat{r})$ is given by

$$\psi_i(\hat{r}) = \phi_{1i}(1)\phi_{2i}(2) \pm \phi_{1i}(2)\phi_{2i}(1).$$

The plus and minus signs refer to the singlet and triplet states respectively. The orbitals $\phi_{ij}(\hat{r})$ are chosen to have the parametric form of the Harris type elliptic orbitals (Harris 1960)

$$\begin{aligned} \phi_{ji}(\hat{r}) = & \exp[\delta_j \xi_j - \rho_j \eta_i] \xi_i^{n_i} \eta_i^{m_i} \exp(iv_j \phi_j) \\ & \times [(\xi_i^2 - 1)(1 - \eta_i^2)]^{|v_j|/2} \end{aligned}$$

Where ξ_i, η_i and ϕ_i are the elliptical coordinates of the i th electron; δ_j, ρ_j, v_j are variables; n_j, m_j are the fixed parameters used for forming higher orbitals. The factor $\exp(iv_j \phi_j)$ determines the orbital angular momentum about the internuclear axis. The properties of these orbitals and evaluation of various integrals using these orbitals have been described by Harris (1960). Since the azimuthal correlation is small (Green 1974, 1978) and the error in the calculated kinetic energy arising from this is negligible (Rama Rao and Chandra 1985), we have chosen only three configurations ($v = 0$) for the description of the ground and the two excited states. Each configuration has nonlinear parameters, $\delta_1, \rho_1, \delta_2$ and ρ_2 which are optimised at each value of R using the Powell-Botm algorithm (Kuester and Mize 1973). Results for the two excited states $[(^1\Sigma)^* \text{ and } (^3\Sigma)]$ are discussed in a previous note (Rama Rao and Chandra 1985). Results for the ground state are as good as those published by Wolniewicz (1965). The wavefunctions of the ground and excited states are available from the author on request.

3. Dynamics of bond formation in the ground state

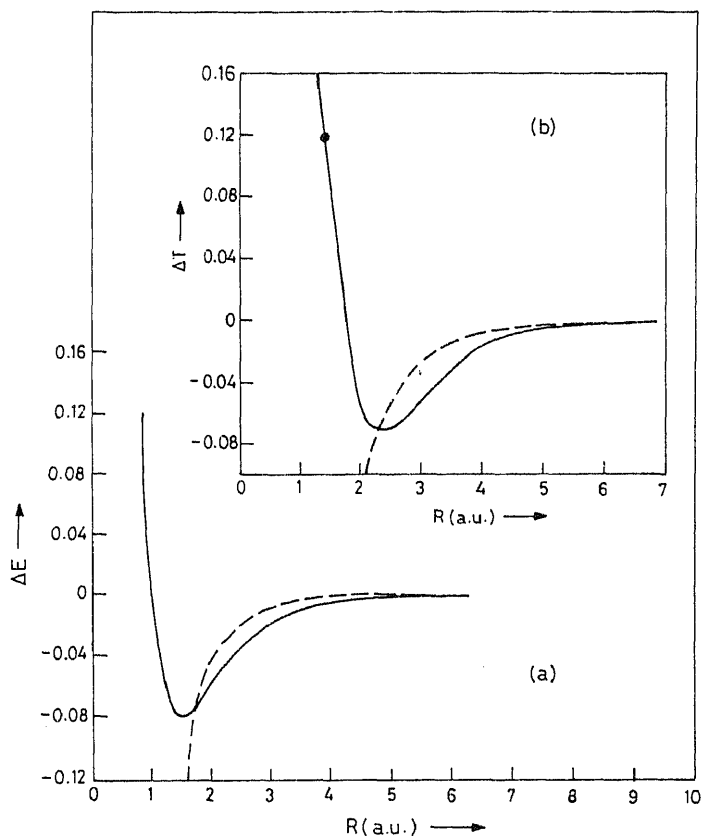


Figure 1. (a) Variation of ΔE with R for the lowest ($^1\Sigma$) state obtained from the *ab initio* wavefunctions. The dashed lines indicate the variation of the classical polarisation energy; (b) Variation of ΔT with R for the lowest ($^1\Sigma$) state. The dashed lines indicate the variation of ΔT according to (5). The black dot indicates the position of the equilibrium R .

variation of the total energy is due to this polarisation alone then by means of the virial theorem the kinetic energy change ΔT can be given by

$$\Delta T(R) = T(R) - T(\infty) = -(3\alpha/2R^4), \quad (5)$$

where $T(R)$ represents the expectation value of the kinetic energy of electrons at R . In figure 1b are shown the variations of ΔT with R , obtained from the *ab initio* wavefunctions of the ground state of HeH^+ , and by the dashed lines, the variation of ΔT according to (5). Both figures 1a and b reveal that at large R the polarisation interaction plays an essential role. The kinetic energy decreases because polarisation tends to expand the space occupied by electrons. As the atoms get closer, a volume exclusion process begins to occur (Matcha and King 1977). Electrons tend to occupy a smaller volume, the uncertainty in the position of electrons decreases and the kinetic energy increases. Therefore formation of HeH^+ can be viewed, in essentially classical

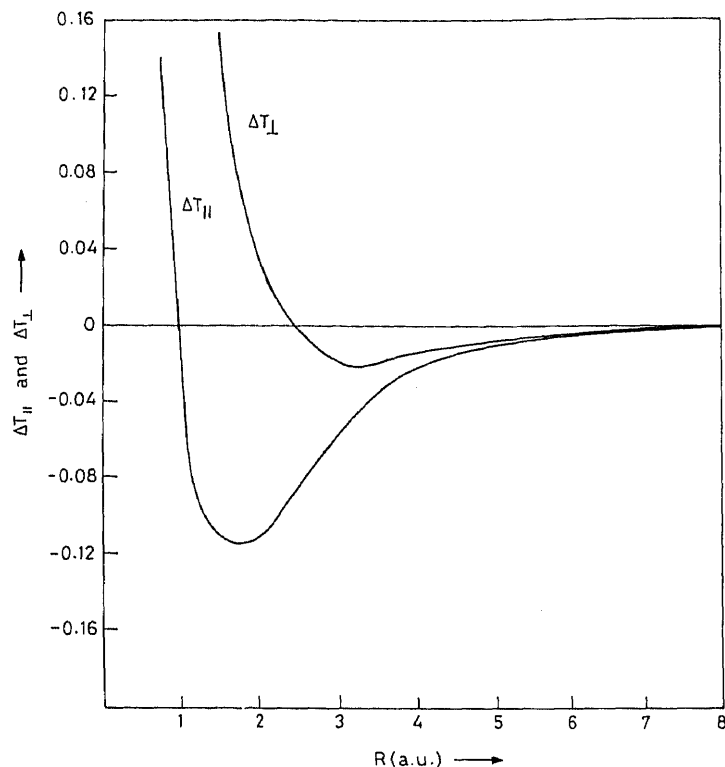


Figure 2. Variations of $\Delta T_{||}$ and $\Delta T_{\perp}$ with R for the lowest (1Σ) state of HeH^+ .

We then consider the geometric partitioning of T as $T_{||}$ (bond-parallel) and $T_{\perp}$ (perpendicular) components. In figure 2 is shown the variation, with R , of $\Delta T_{||}(R) [i.e. T_{||}(R) - T_{||}(\infty)]$ and $\Delta T_{\perp}(R) [i.e. T_{\perp}(R) - T_{\perp}(\infty)]$ for the ground state. The $T_{||}(\infty)$ and $T_{\perp}(\infty)$ are taken as $1/3$ and $2/3$ times respectively, the atomic kinetic energy. If $\Delta T(R)$ be given by (5) then one expects for the polarisation effect alone

$$\Delta T_{||}(R) = 1/2 \Delta T_{\perp}(R) = -(\alpha/2R^4).$$

Figure 2 shows, however, that the magnitude of $\Delta T_{||}(R)$ at large R is large $\Delta T_{\perp}(R)$, contrary to the expectations from (6). $\Delta T_{\perp}$ decreases initially very slowly then increases rather rapidly while $\Delta T_{||}$ continues to decrease until $R = 1.8$ au, and then begins to increase. According to Ruedenberg's analysis (Ruedenberg 1975; Feinberg and Ruedenberg 1971) of H_2^+ , this increase of $T_{\perp}$ and decrease of $T_{||}$ as the atoms get closer to each other arise from the interference effect.

The interference effect in HeH^+ can arise from the charge transfer from the neutral He atom to H^+ in the following way. We consider the following approach

and 'a' and 'b' are the Slater type 1s orbitals of He and H, respectively. Using wavefunction (7), one obtains

$$\langle T \rangle = [2T_a + \lambda^2(T_a + T_b) + 2\lambda(T_a \langle a|b \rangle + \langle a|\hat{T}|b \rangle)]/[1 + \lambda^2 + 2\lambda \langle a|b \rangle] \quad (9)$$

$$\Delta T = \langle T \rangle - T_{\text{He}} \approx 2\lambda[\langle a|\hat{T}|b \rangle - T_a \langle a|b \rangle], \quad (10)$$

where $T_a = 1.44$ au, since $\Delta T = \Delta T_{\parallel} + \Delta T_{\perp}$ one can write:

$$\Delta T_{\parallel}(R) \approx 2\lambda[\langle a|\hat{T}_{\parallel}|b \rangle - 0.48 \langle a|b \rangle], \quad (11)$$

$$\Delta T_{\perp}(R) \approx 2\lambda[\langle a|\hat{T}_{\perp}|b \rangle - 0.96 \langle a|b \rangle]. \quad (12)$$

These two-centre kinetic energy integrals involving 1s orbitals are discussed by Ruedenberg (Feinberg and Ruedenberg 1971; Ruedenberg 1975) and also by Baumann and Heilbronner (1966). They have shown that at large R , $\langle a|\hat{T}_{\parallel}|b \rangle$ decreases and $\langle a|\hat{T}_{\perp}|b \rangle$ increases with decreasing R . Equations (11) and (12) can qualitatively explain the large initial decrease of $\Delta T_{\parallel}$ while the initial increase of $\Delta T_{\perp}$ is cancelled by the second term of (12). This analysis therefore suggests that the bond-formation in the lowest ($^1\Sigma$) state of HeH^+ arises from the interference effect following the flow of charge from He to H^+ . The bond-formation is not preceded by the classical polarisation of He by H^+ . This is not surprising as the polarisability of He is very small. Politzer (1966) argued that the charge-transfer from He to H^+ is difficult as the ionisation potential of He is high. But when a positive ion approaches a neutral atom the high ionisation potential of the neutral atom can be overcome by the attractive energy of the electron with the approaching positive ion (i.e. $-e^2/R$).

4. Electron densities on the atoms in HeH^+ ($^1\Sigma$)

Butscher and Schmidtke (1978) partitioned the total molecular electron density into quasi classical, q^c and interference, q^i terms. When the interference term is integrated over all space, it gives zero, while q^c of the atom gives the number of electrons in the atom. They found that for the nearly dissociated system ($R = 10$ au), $q(\text{He}) = 1.9999$ and $q(\text{H}) = 0.0001$ (see table 3 of Butscher and Schmidt 1978). This result indicates that even at large R , charge migration has taken place. They have used Slater-type orbitals on each atomic centre. It is not possible with elliptic orbitals to partition the total density into the quasi-classical and interference terms. We have calculated the density on the H and He nuclei in HeH^+ as a function of R . They are denoted by $\rho_{\text{H}}(R)$ and $\rho_{\text{He}}(R)$ in figures 3a and b. In the same figure (3a) the density of the He atom, q_{He} as a function of R from the nuclear centre is shown. These densities are obtained from the wavefunction of the He atom given by Silverman *et al* (1960). Figures 3a and b, show that the density on the H-nucleus is always greater than that expected from the classical penetration of a proton into the undeformed charge cloud of He. On the other hand, figure 3b shows that as R is decreased, the density on the He nucleus decreases. These results corroborate our findings from kinetic energy studies that charge-transfer from He to H^+ takes place before the bond is formed. But these results do not completely rule out the possibility of polarisation of He by H^+ . As the He atom is polarised, density on the He nucleus should decrease while the tail of the He atom wavefunction should increase toward the proton causing a rise in density on the proton centre. It should be

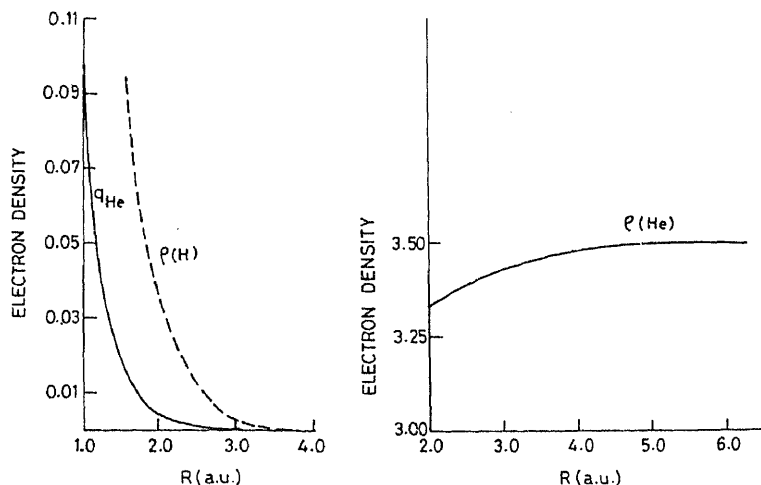


Figure 3. The variation of $\rho(\text{H})$ and $\rho(\text{He})$ in the lowest ($^1\Sigma$) state of HeH^+ with R . The variation of the free atom density of He, q_{He} with R from the nuclear centre is also shown.

noted that the analysis of the $T_{\parallel}$ and $T_{\perp}$ components (figure 2) can unequivocally reveal that bonding in HeH^+ is not preceded by polarisation.

5. Dynamics of bond-formation in the first excited, i.e., ($^1\Sigma$)* and the lowest ($^3\Sigma$) states of HeH^+

Our *ab initio* calculations on these two states of HeH^+ show that both dissociate into He^+ and H and exhibit weak bonding. Our calculations further reveal that the ($^3\Sigma$) state is about 2.3 times more stable than the ($^1\Sigma$)* state. In figure 4 are shown the variations of $\Delta T(R)$ with R calculated from the *ab initio* wavefunctions of the ($^1\Sigma$)* and ($^3\Sigma$) states. At large R , the H-orbital is expected to be polarised by He^+ and $\Delta T(R)$ obtained from the classical polarisation is shown in the same figure by the dashed lines. The polarisability α of the H atom is $4.5 a_0^3$. At large R , the kinetic energy change is the primary contributor to the long-range attractions. If bond formation in the ($^1\Sigma$)* and ($^3\Sigma$) states of HeH^+ is preceded by polarisation then in the initial stage kinetic energy should decrease as shown in figure 4 because polarisation tends to expand the space where the electrons move. Figure 4 gives therefore an impression that the weak bonding in these two states of HeH^+ is due to ion-induced dipole attraction. Since bond energies of these weakly bound states are in the range of 1–2 kcal/mol and the polarisation energy is also of the same order near $R \sim 5.0$ Bohr, such inference has not been called into question.

We then consider $T_{\parallel}$ and $T_{\perp}$. In figure 5 are shown the variations with R of $\Delta T_{\parallel}$ and $\Delta T_{\perp}$ for the ($^1\Sigma$)* and ($^3\Sigma$) states. Figure 5 shows again that $\Delta T_{\perp}$ slowly increases from zero while $\Delta T_{\parallel}$ decreases. Thus the bond formation in these two states is not

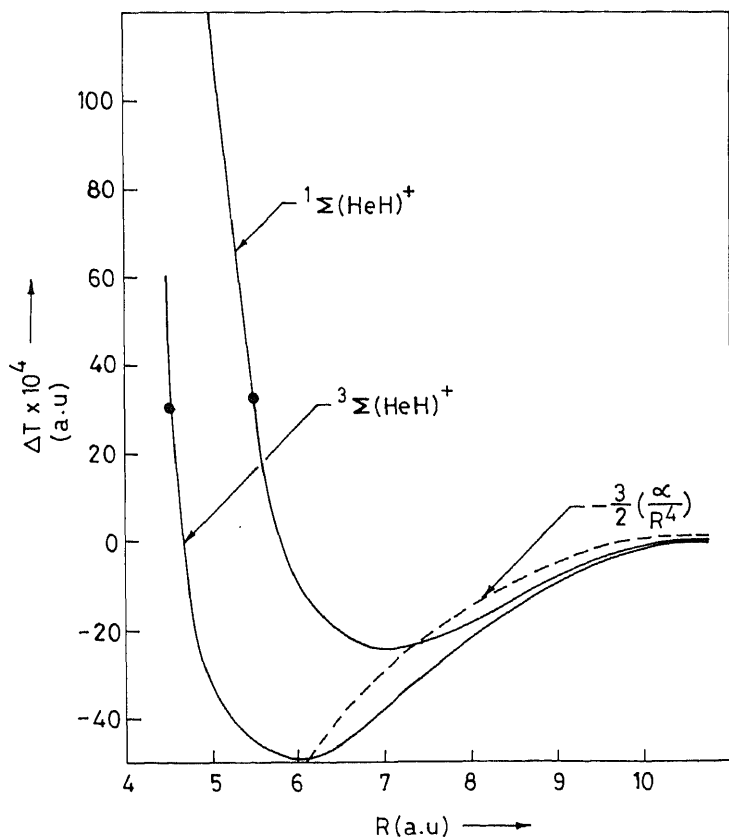


Figure 4. Variation with R , of ΔT for the first excited (1Σ)* and the lowest (3Σ) states of HeH^+ . The dashed lines indicate the variation of ΔT obtained from classical polarisation.

charge-transfer and hence a larger initial lowering of ΔT (and $\Delta T_{\parallel}$) is expected for the 3Σ state. Thus the difference in bonding in these two excited states of HeH^+ arises from the different extent of charge-transfer from H to He^+ .

The density and density difference maps of HeH^+ in its first excited (1Σ)* and (3Σ) states

et al (1956) had earlier introduced the definition of the charge density difference function as

$$\Delta\rho(\hat{r}) = \rho_m(\hat{r}) - \rho_a(\hat{r}) \quad (13)$$

the difference in the distribution of electronic charge density between that found in the molecule, $\rho_m(\hat{r})$ and that obtained by the superposition of the unperturbed atomic charge densities $\rho_a(\hat{r})$. The $\rho_a(\hat{r})$ is expressed as a sum of the contributions from each of the isolated atom densities, the nucleus of each atom occupying a position identical to its position in the molecular system. Contour maps of $\rho_m(\hat{r})$ and $\Delta\rho(\hat{r})$ display the densities

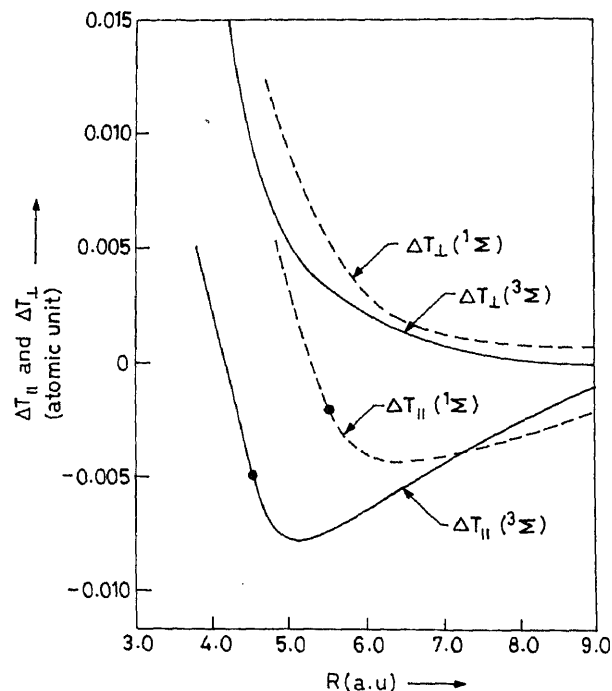


Figure 5. Variation of $\Delta T_{||}$ and $\Delta T_{\perp}$ with R for the first excited (1Σ)* and lowest (3Σ) of HeH^+ .

and the change of densities that occur during the formation of molecules.

The total molecular density distributions $\rho_m^{(p)}$ for the (1Σ)* ($R_e = 5.5$ Bohr) (3Σ) ($R_e = 4.5$ Bohr) states of HeH^+ are shown in figure 6. The first contour envelop both the nuclei in HeH^+ has a value less than or equal to 0.005. A contour of higher density is closed separately around each nucleus. Thus the portion of the total electron density is centred on the nuclei in both the states. The very different from the ρ_m -map of the ($1\Sigma_g^+$) state of H_2 (Wahl 1966) where even contours of values larger than 0.01 encompass both the nuclei at R_e indicating a sharing of electrons.

In figure 7 are shown $\Delta\rho$ -maps for the (1Σ)* and (3Σ) states of HeH^+ at the indicated values of R . Figure 7 shows the deformation of density around the H-nucleus towards the He nucleus. This deformation could arise from polarisation of the H-atom by the He nucleus or by charge transfer from H to He^+ . The negative $\Delta\rho$ region behind the H-nucleus is indicative of charge transferred from behind the H-nucleus. As R is decreased, there is no indication of a single contour line of positive $\Delta\rho$ enveloping both nuclei corresponding to a shared density as in H_2 (Bader and Chandra 1968). In both the (1Σ)* and (3Σ) states, the distribution of charge transferred from hydrogen is accumulated on the H-side of the internuclear region. This leads to unsymmetrical distribution of charge in the internuclear region. The charge build-up in the internuclear region in the first excited (1Σ)* and the lowest (3Σ) states does not therefore arise from the same mechanism of electron sharing observed in H_2 . This unsymmetrical charge distribution can be understood more easily in terms of Slater type orbitals. When the 1s orbitals of

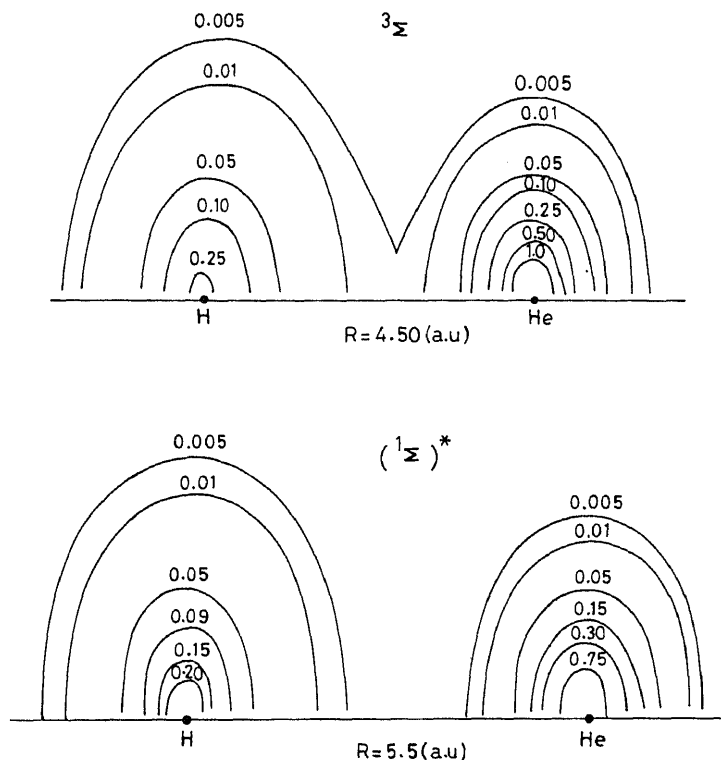


Figure 6. Density contour maps for the $(^1\Sigma)^*$ and $(^3\Sigma)$ states at their respective R_e values.

are brought closer, electrons cannot exchange as in H_2 because these two differ in energy by 40 eV. Since the $2s$ orbital of He^+ is degenerate with the $1s$ of H, on closer approach the electron of H can move to the $2s$ orbital of He^+ . $1s$ - $2s$ overlap leads to unsymmetrical charge distribution in the internuclear region also responsible for the observation of interference effect at larger R . distribution of charge in a chemical bond must account for the electrostatic y. Since the charge is heavily concentrated on the proton side of the internuclear the force exerted on the He nucleus by this density is so great that the He nucleus each electrostatic equilibrium only by having its own density polarised away from atom. This is the origin of the negative $\Delta\rho$ near the He nucleus in the internuclear

conclusions

y, therefore, conclude that in both the ground and excited states of HeH^+ the ation of the neutral atom orbitals by the positive ion is not important even at , contrary to earlier beliefs. Bond formation in these states is preceded by charge- from the neutral atom to the positive ion. The interference effect following the

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Diabatic energy surface for H_3

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Abstract. The form of the diabatic energy surface for the H_3 system is considered. It does not have the full permutation symmetry of the nuclei. The diabatic crossing and the conical intersection are compared. A fit to the calculated points of Siegbahn and Liu using the exponential map is described and the results discussed.

Keywords. Diabatic potential energy surfaces; H_3 energy surface; fitting of potential energy surfaces.

Introduction

To investigate the dynamics of a molecular reaction it is first necessary to have a representation of the electronic energy of the molecule as a function of its nuclear configuration. The energy for selected configurations may be obtained from an *ab initio* calculation and some neighbourhoods may be known through analysis of vibration spectra; so, the problem is to fit these data into a formula which extrapolates the energy to other configurations. An extensive account of existing techniques for this purpose has been given by Murrell *et al* (1984).

In a previous publication (Hall and Okada 1985) the authors have proposed a new representation for the energy and illustrated it by fitting the H_3 data of Siegbahn and Liu (1978). The internuclear distances R_1, R_2, R_3 are replaced by their exponential representations:

$$X = \exp(-aR_1); Y = \exp(-aR_2); Z = \exp(-aR_3), \quad (1)$$

The energy is represented as a power series

$$V(X, Y, Z) = \sum_{r,s,t}^{r+s+t \leq n} V_{rst} X^r Y^s Z^t. \quad (2)$$

The coefficients V_{rst} and the scale factor a are fitted by a least squares procedure. The atomic limit, which has $Y = Z = 0$, is fitted first and the series then gives a natural generalization of the Morse potential

$$V(X, 0, 0) = \sum_{r=0}^n V_{r00} X^r. \quad (3)$$

The remaining coefficients are fitted to the triatomic *ab initio* calculated points. To maintain the symmetry of the energy surface the coefficients must satisfy full

permutation symmetry:

$$V_{rst} = V_{srt} = V_{rts} \quad \dots \quad (4)$$

This condition reduces the number of independent coefficients very considerably. An advantage of the form (2) is that it combines the diatomic data with the triatomic data smoothly and enables them to be determined independently. Since it does not appeal to any physical consideration to include terms of a special form it is more suited to general application, but it will require more terms to achieve a given accuracy of fit, than procedures that do take advantage of these considerations.

Most molecular calculations are based on the Born-Oppenheimer separation of the electronic motion from the nuclear motion and, in particular, restrict the electronic wavefunction to a representation of the space and spin symmetry of the Born-Oppenheimer Hamiltonian. When the energies of two different states become close these adiabatic surfaces may not be the most useful nor the most significant ones to find. It has been argued that the diabatic surfaces (Lichten 1963) have greater physical importance. For a review see O'Malley (1971). A diabatic surface for H_2O has been given by Murrell *et al* (1981) and one for O_3 by Carter *et al* (1982). In this paper the calculation of a diabatic surface using the exponential map will be demonstrated. It is convenient to use H_3 as an example again since this facilitates comparisons with previous work and since a diabatic surface for this system has many interesting aspects.

2. Symmetry breaking

It is not easy to give a rigorous definition of the diabatic energy since it is not the solution of an eigenvalue equation as the adiabatic energy is. As an energy, it is a smooth interpolation between an energy which is on the lower surface on one side of a crossing point and the upper surface on the other side. It is easier to define it as the mean energy of an approximate wavefunction which retains its character through the crossing. Near the crossing the adiabatic wavefunction will mix this wavefunction with the second diabatic one which crosses in the opposite direction.

One of the differences between diabatic and adiabatic wavefunctions is the treatment of symmetry. The adiabatic wavefunction must belong to an irreducible representation of the molecular symmetry group of the configuration and its energy surface must be fully symmetrical. The diabatic one need not. To have the correct relation to the adiabatic wavefunction the diabatic one, together with the second diabatic one which it crosses, should, as a pair, span one or two irreducible representations. This is a significant relaxation of the symmetry condition and implies that neither diabatic energy surface need be fully symmetrical though the two surfaces together must be. In a typical diabatic wavefunction some atoms are bonded and some are not. This bonding will be appropriate to the ground state for configurations in which these atoms are suitably placed but, for configurations which bring other atoms together, it may correspond to an upper state since there is another, more appropriate, choice of bonds. For H_3 it is readily shown that the equilateral configurations have spatially doubly-degenerate wavefunctions so that the two surfaces do cross there. This conical intersection has been discussed by Teller (1937) and by Herzberg and Longuet-Higgins (1963). The adiabatic surface has then a cusp at these equilateral points whereas the diabatic surface has a smooth crossing

The implication for the fitting process of this symmetry breaking is considerable. To fit a cusp using analytic functions means rather slow convergence and this is what was found in the previous fitting. By eliminating the cusp the fitting should be more rapid. Furthermore, the reduction in symmetry increases the number of independent coefficients available for fitting and hence improves the fitting which is possible using terms of up to a given degree.

3. The shape of the H_3 diabatic surface

The H_3 system has some special features which arise from its three-fold symmetry and the space and spin properties of its states. These must be reflected in the fitted surfaces.

Since two surfaces cross at equilateral configurations there must be two energy states at all configurations. In the diatomic limit these two states are the ground state and the lowest triplet state of H_2 , the bonding and the anti-bonding states. Both of these are known from accurate calculation, so the fitting must now include both.

In collinear configurations the two neighbouring atom pairs should be treated in the same way since both are partly bonded, and become fully bonded when the third atom retreats far away. It is the interaction between the extreme atoms which is distinguished from these and becomes the anti-bonding interaction. As the third atom retreats, its bonding and anti-bonding interactions tend to cancel, so releasing it from the molecule. Thus, the diabatic surface will retain the permutation symmetry of the first pair of atoms but break their symmetry with the third atom.

In an equilateral configuration the diabatic wavefunction will have two pairs of atoms bonded and the third anti-bonded. This will obviously have the same energy as that of the wavefunction which has a different choice for the third pair and so their energy surfaces will cross in this configuration. The second wavefunction can be derived from the first by applying a permutation to it. This permutation is one of those missing from the wavefunction and ensures that the two functions together span a degenerate representation of the full permutation group. This means that only one energy form is required to specify both diabatic surfaces. This self-intersection is a special feature of the H_3 system.

4. The fitting procedure

The suggested form for the diabatic energy surface is

$$V = \sum_{r,s,t=0}^{r+s+t \leq n} V_{rst} X^r Y^s Z^t, \quad (5)$$

where, now, the variables are

$$X = \exp(-aR1), Y = \exp(-aR2), Z = \exp(-bR3) \quad (6)$$

and the symmetry is

$$V_{rst} = V_{srt}. \quad (7)$$

When $R2 \leq R3$ and $R1 \leq R3$ this is the energy of the lower surface and when $R3 \leq R2$

$$V(X, 0, 0) = \sum_{r=0}^{\infty} V_{r00} X^r \quad (8)$$

to fit to the energy of the ground state of H_2 . The triplet state energy of H_2 is similarly fitted to the other diatomic limit

$$V(0, 0, Z) = \sum_{i=0}^n V_{00i} Z^i \quad (9)$$

and the scale factor b found. Both surfaces then have their correct asymptotic form.

The triatomic points whose energies were calculated by Siegbahn and Liu (1978) already have $R_1 \leq R_2 \leq R_3$ so they can be fitted to the lower surface form without any modification. The least squares procedure gives the coefficients V_{rst} as the solution of a set of linear equations. This assumes that the diabatic and adiabatic surfaces remain very close together at all points used in the fitting and differ only when extrapolated beyond the crossing.

In fact, the diabatic energy surface differs from the adiabatic one in one major respect. It gives a crossing of the diabatic energies for any isosceles configuration $R_2 = R_3$. This is not required by the symmetry of the system, so it is a diabatic crossing and not an adiabatic one. It is a two-dimensional crossing (any $R_1, R_2 = R_3$) whereas the adiabatic crossing is one-dimensional ($R_1 = R_2 = R_3$). Such a difference in the crossing is exactly what is expected but it complicates the fitting process because, near such crossing, the adiabatic points should not be used to fit the diabatic surface. Since the equilateral configuration does have a crossing, the points that should be avoided are ones close to $R_2 = R_3$ and with R_1 rather different. One such point was readily identified in the Siegbahn and Liu list (at 0.9, 2.64, 3.449). These points can be identified more quantitatively by finding the separation between upper and lower surfaces at each point and selecting those which are close. After these near-crossing points have been identified the fitting of the remaining points must be repeated. This should result in an improved fitting.

The near-crossing points can also be analysed. At these the adiabatic energies can be defined as the eigenvalues of a 2×2 matrix whose diagonal elements are the diabatic energies for upper and lower surfaces. The off-diagonal element is a new variable. Thus, with the upper and lower energies

$$V_u = \sqrt{\frac{1}{3}} (V(X, Z, Y) - V(Z, Y, X)), \quad V_l = V(X, Y, Z), \quad X \geq Y \geq Z, \quad (10)$$

and the interaction element U , the matrix

$$\begin{pmatrix} V_u & U \\ U & V_l \end{pmatrix} \quad (11)$$

has eigenvalues

$$E_{\pm} = \frac{1}{2}(V_u + V_l) \pm \frac{1}{2}\{(V_u - V_l)^2 + 4U^2\}^{\frac{1}{2}}. \quad (12)$$

The interaction U will also depend on configuration. Since it connects two wave-functions which permute either into themselves or into one-another it must be fully symmetric. Since the diatomic limits are already accurately fitted, U must vanish at these limits. It must also vanish for equilateral configurations. These conditions imply

that the first non-zero term in the expansion of U will be

$$U = u(X^2Y + Y^2Z + Z^2X + X^2Z + Y^2X + Z^2Y - 6XYZ), \quad (13)$$

where u is a constant. This constant can be fitted using the near-crossing points previously omitted from the diabatic fitting and the eigenvalue formula (12). This U is not a part of the diabatic fitting itself but it is relevant to it since it features in calculations that use the diabatic energy concept.

5. Results for H_3

The procedure described above was applied to H_3 . The very accurate calculations of Kolos and Wolniewicz (1965) were used for the diatomic limits (8) and (9). Next, all points given by Siegbahn and Liu were fitted to the diabatic form (5). As suggested by Truhlar and Horowitz (1978), these energies were depressed by 0.001167 h to make the bottom of the channel join smoothly with the molecular minimum. This was repeated for terms of up to the n th degree for $n = 2, \dots, 8$. The root mean square (RMS) error of these fittings is shown in figure 1 with the label Dia(156). It may be compared with the corresponding RMS error for the adiabatic fitting given in the earlier paper and labelled Adi. With the exception of the fitting for $n = 3$, the improvement in fitting is evident.

Next, the point mentioned above as a near-crossing point was removed from the list and the fittings were repeated. The RMS errors for these are shown in figure 1 with the label Dia(155). For $n > 6$ the improvement in fitting is dramatic. As the fitting improves so these near-crossing points limit the accuracy obtainable and their removal allows the truly diabatic points to be fitted more closely. When the energies of both states were calculated this special point did indeed emerge as close to the crossing. Three other points were also identified as near-crossing points and removed from the list of fitting. When the fitting was repeated there was a further improvement in accuracy, but a very modest one.

As a fitting process this procedure is far from ideal. The upper surface contributes no points, apart from the diatomic limit, so the fitting can do anything there. Inspection of the results of this fit suggests that the results are quite unreliable for the upper surface away from the crossing points. The procedure for finding u also proved to be difficult because it was highly sensitive to the remaining errors in what was already a good fit. Furthermore, the fitting process ensures that the diabatic surface will overestimate some adiabatic points and underestimate others. However, the use of the eigenvalues (12) assumes that the diabatic surface is always above the adiabatic one for the lower surface and below it for the upper one. This contradiction indicates the need for some feed-back between the two calculations but a suitable one was not found. A least squares fit of u at the same time as the other coefficients would have led to much more complicated non-linear calculations and the risk of numerical instability.

The coefficients of the best fitting for $n = 8$ using 155 points are given in table 1.

6. Conclusion

The fitting of a diabatic energy formula to a calculated adiabatic energy surface involves some difficult problems and some major advantages. Since, by definition, the diabatic

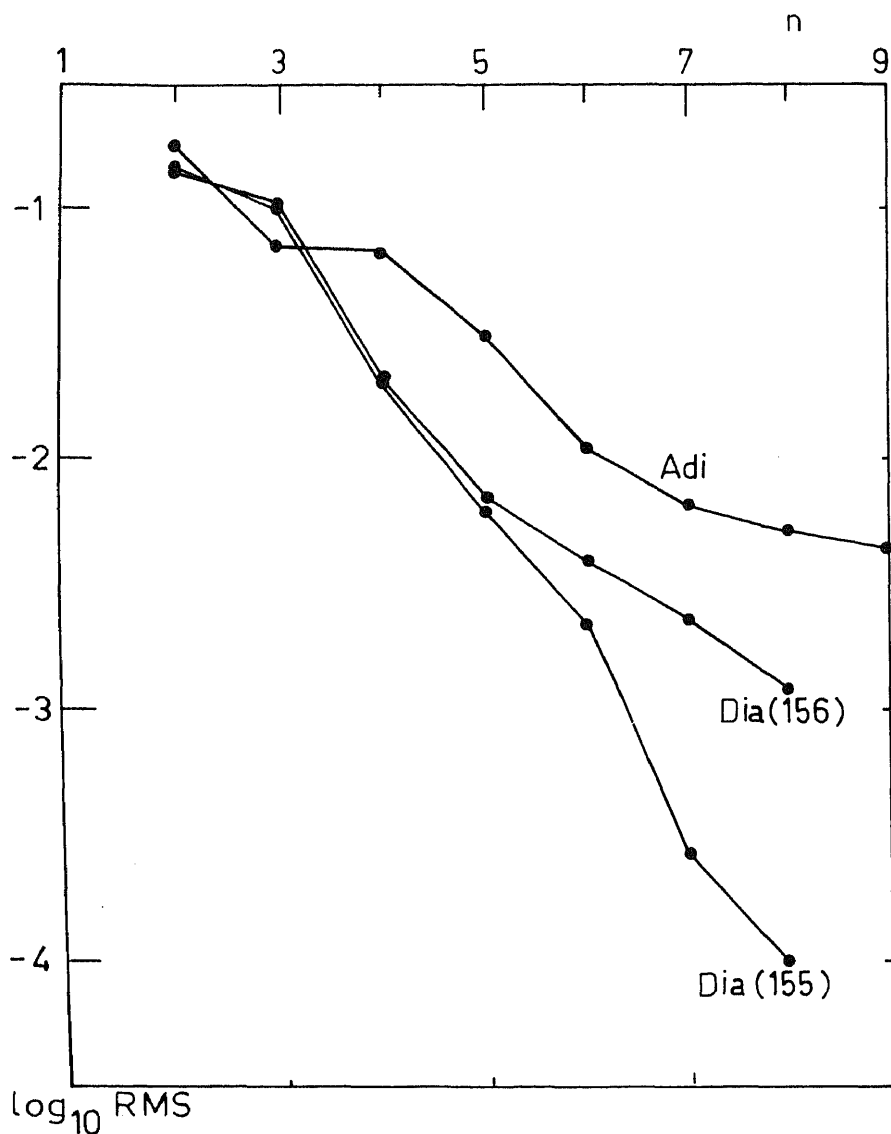


Figure 1. The logarithm of the RMS error of fitting as a function of n , the highest degree terms included. Adi labels the adiabatic fitting and Dia the diabatic ones.

surface is a smooth interpolation between two adiabatic states it eliminates the cusps in the adiabatic surface which make the fitting of that energy so slow. On the other hand, there is no clear division between the points that belong to the diabatic surface and those that are in the crossing region and so should be excluded from the fitting. The procedure used above, of dividing the points according to the closeness of the surfaces, is clearly crude and does lead to difficulties.

Table 1. Coefficients of the diabatic energy for H_3 . The index is equated to the value in hartrees. The exponent is in parenthesis.

$a = 0.583788900$		$b = 0.536200000$
100 = -0.712085069 (-3)	001 = -0.856672657 (-3)	
200 = -0.132995913 (-1)	002 = -0.146339662 (0)	110 = 0.401040427 (1)
101 = -0.394985046 (1)		
300 = -0.333406637 (2)	003 = 0.829644260 (1)	210 = -0.417463883 (2)
201 = 0.154860307 (3)	102 = -0.189891297 (2)	111 = -0.886436238 (2)
400 = 0.210403701 (3)	004 = -0.329153955 (2)	310 = 0.223632902 (3)
301 = -0.157813687 (4)	103 = -0.809781429 (3)	220 = 0.724597086 (3)
202 = 0.200875280 (4)	211 = -0.462795459 (3)	112 = 0.239991159 (2)
500 = -0.611635040 (3)	005 = 0.887681408 (2)	410 = -0.162302758 (3)
401 = 0.597013137 (4)	104 = -0.226013080 (5)	320 = -0.488308306 (4)
302 = -0.102837946 (5)	203 = 0.200888630 (5)	311 = 0.731273207 (4)
113 = 0.882282274 (5)	221 = 0.316201689 (5)	212 = -0.543631675 (5)
600 = 0.975465474 (3)	006 = -0.155141866 (3)	510 = -0.689010998 (3)
501 = -0.108764381 (5)	105 = -0.208392950 (6)	420 = 0.310058104 (4)
402 = 0.519856651 (4)	204 = 0.233024233 (6)	411 = -0.368729470 (4)
114 = 0.106039695 (7)	330 = 0.433921190 (5)	303 = -0.513385250 (5)
321 = -0.195230475 (6)	312 = 0.278278426 (6)	213 = -0.101258881 (7)
222 = 0.817930862 (6)		
700 = -0.818267260 (3)	007 = 0.149210364 (3)	610 = -0.786701725 (3)
601 = 0.122602001 (5)	106 = -0.603599450 (6)	520 = 0.161238338 (5)
502 = -0.782001816 (3)	205 = 0.131715362 (7)	511 = -0.960138027 (4)
115 = 0.313676085 (7)	430 = -0.592397704 (5)	403 = 0.139585866 (6)
304 = -0.846477798 (6)	421 = 0.255141582 (6)	412 = -0.462108545 (6)
214 = -0.460963505 (7)	331 = 0.617444450 (6)	313 = 0.256186586 (7)
322 = -0.203336853 (7)	223 = 0.489785900 (7)	
800 = 0.287217386 (3)	008 = -0.538825542 (2)	710 = 0.268464941 (4)
701 = -0.753144931 (4)	107 = -0.267023381 (6)	620 = -0.132386778 (5)
602 = 0.253282624 (5)	206 = 0.126345705 (7)	611 = -0.141847397 (5)
116 = 0.128913578 (7)	530 = -0.382608799 (4)	503 = -0.256779051 (6)
305 = -0.189733379 (7)	521 = -0.766267203 (5)	512 = 0.384248761 (6)
215 = -0.326312916 (7)	440 = 0.144150579 (5)	404 = 0.113307128 (7)
431 = -0.125577742 (6)	413 = -0.202936209 (7)	314 = 0.388730910 (7)
422 = 0.940706903 (6)	224 = 0.386141761 (7)	332 = 0.808547638 (6)
323 = -0.267002284 (7)		

closely. The RMS error of the fitting in table 1 is 0.06 kcal/mol and the maximum deviation from the Siegbahn and Liu points is 0.31 kcal/mol. These are significantly smaller than those of the Truhlar and Horowitz (1978) fitting. As a representation of the calculated points, this fitting can have its uses. The upper surface, which is simply derived from the first by a permutation of variables, is not fitted to any calculated point and is not significant. An *ab initio* calculation of some points on this surface would be

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Absorption spectrum for the transition state $H_3^\ddagger$ —A quantum mechanical model study

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Abstract. The absorption spectrum for the transition state in the collinear reaction $H + H_2 \rightarrow H_3^\ddagger \rightarrow H_2 + H$ is predicted, using the time-independent Schrödinger equation for a model consisting of a one-dimensional rectangular potential barrier and a well.

Keywords. Absorption spectrum; transition state; quantum mechanical study.

Introduction

In recent years, the possibility of a direct spectroscopic observation of transient species which are intermediate between reactants and products, usually referred to as the transition state (ts) or reaction complex, has triggered off a lot of research (Polanyi 1973; Foth *et al* 1982). Arrowsmith *et al* (1980, 1983) reported the emission spectrum of the transition state for the reaction,



by monitoring the wings to the sodium *D*-line emission. Polanyi and Wolf (1981) and Arrowsmith *et al* (1982) interpreted the wings as arising from the emission from Na^* while the separating NaF is still in the vicinity. Brooks and coworkers (Hering *et al* 1982; Brooks *et al* 1982; Maguire *et al* 1983) have reported evidence for absorption from the transition state in reactions:



Interest in the ts spectroscopy stems from the fact that it may provide some glimpse of the reactive potential-energy surface (pes) in the region crucial to the determination of the outcome of a molecular collision, complementary to the results from state-to-state chemistry (Brooks and Hayes 1977) which focusses attention on reactants and products, thus yielding only indirect information about the structure of the reaction complex.

It is thus of fundamental interest to interpret the wings to the Lyman- α absorption in $H + H_2$ collisions. Polanyi and coworkers (Mayne *et al* 1984a) computed the absorption spectrum for the ts of the collinear reaction



by determining the probability density distribution for the TS on the chem accurate Siegbahn-Liu-Truhlar-Horowitz (SLTH) (Liu 1973; Siegbahn and Liu Truhlar and Horowitz 1978, 1979) *ab initio* PES using the quasi-classical trajectory technique. They assumed vertical transitions from the ground state to one of the lying excited states that correlates with $H^*(2p) + H_2$. They found that as the collision energy increased, the intensity of the spectrum diminished and there was a considerable red shift for the wings to the Lyman- α line. Subsequently they extended (Mayne 1984) their study to collisions in three dimensions using a diatomics-in-molecules potential energy surface for the upper state, and concluded that the qualitative features of the spectrum remained invariant while going from collinear geometry to three dimensions.

Engel *et al* (1985) have carried out time-independent quantum mechanical calculations and predicted the absorption spectrum for the collinear reaction (R4) for two different vibrational states ($v = 0$ and $v = 1$) of the hydrogen molecule at collision energies below the reaction threshold, using the same PES as Polanyi and coworkers did. The QM and QCT results were compatible as far as the basic trends were concerned.

Recently Agrawal *et al* (1985) have reported results of a time-dependent quantum mechanical treatment of the collinear reaction (R4) for $v = 0$ and $v = 1$ at two different collision energies that are well above the reaction threshold, thus complementary to the results of Engel *et al* (1985).

Here we report the results from a time-independent QM calculation of the absorption spectrum for the same reaction, using a simple model mimicking the relevant potential energy surface. Calculations have been carried out for collision energies both above and below the reaction threshold.

2. Details of the model

The correlation diagram for the first few electronic states of H_3 is given elsewhere (Mayne *et al* 1984a). We reproduce schematically the potential-energy profile along the reaction coordinate for the collinear ($H + H_2$) collision, for the ground state and one of the excited states that correlates with $H^*(2p) + H_2$, in figure 1. We have constructed a simple model in terms of a rectangular barrier and a well with the height and the depth of the well from Mayne *et al* (1984a) as shown by dashed lines in figure 1. We imagine the collision event to be as follows: a plane wave with a specified energy E approaches the barrier. If E is less than the barrier height, it is scattered, thus in part reflected, and in part transmitted. Further, one argues that if E is being scattered, part of it leaks into the upper PES (the square well) and gets caught in one of its bound states. We assume vertical transitions from the ground state to the excited bound state and calculate the spectrum for different values of collision energy. An advantage of this model rests with the fact that the collision energies are kinematically resolvable.

The exercise has been executed in three parts: (1) the rectangular well problem, (2) the rectangular barrier problem, and (3) the intensity calculation.

Eigenvalues and eigenfunctions for the bound states of the potential well are obtained via the graphical technique, as described by Schiff (1968), for example. The wavefunction for the scattering off the barrier is determined by matching the

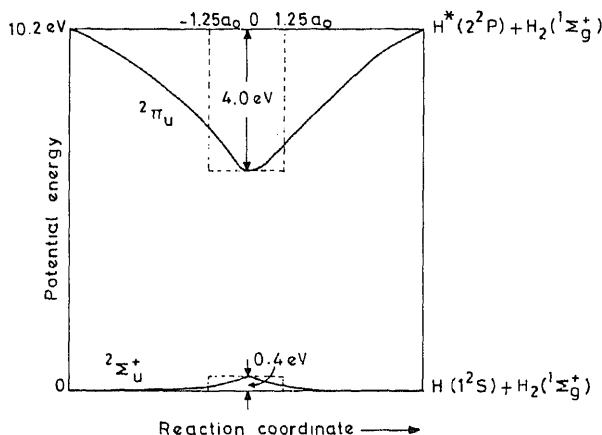


Figure 1. Representation of the potential-energy profile along the reaction path for the collinear collision of $H(H^*) + H_2$. The dashed lines indicate the truncated model used in this study.

For absorption from the ground state (barrier) to the excited state (well),

$$\text{intensity of spectral lines} \propto |\langle \psi_e | \mu | \psi_g \rangle|^2 \quad (1)$$

where μ is the electronic transition moment. In the absence of any available information on μ , the above matrix element can still be estimated roughly by noting that

$$|\langle \psi_e | \mu | \psi_g \rangle|^2 \propto \frac{|\langle \psi_e | \psi_g \rangle|^2}{\Delta E}, \quad (2)$$

where ΔE is the energy difference $E_e - E_g$. Earlier workers (Mayne *et al* 1984a; Engel *et al* 1985; Agrawal *et al* 1985) had also used the same approach. Since the algebra of evaluating the above matrix elements is straightforward, we only give the final results of the intensity calculation.

3. Results and discussion

Absorption spectra of the rs obtained at three different E values are given in figures 2–4 which clearly demonstrate the presence of wings to the Lyman- α line in each case. These wings terminate at frequencies corresponding to transition from the ground state to the highest bound excited state (at the high frequency end of the spectrum) and corresponding to transition from the ground state to the lowest bound state (at the low frequency end of the spectrum). The frequency range over which the spectra extend compares well with its classical counterpart shown in figure 4 of Mayne *et al* (1984a). Our model also leads to the same conclusion as the other detailed studies (Mayne *et al* 1984a; Engel *et al* 1985; Agrawal *et al* 1985) that the red-shifted wing becomes more intense with increase in E .

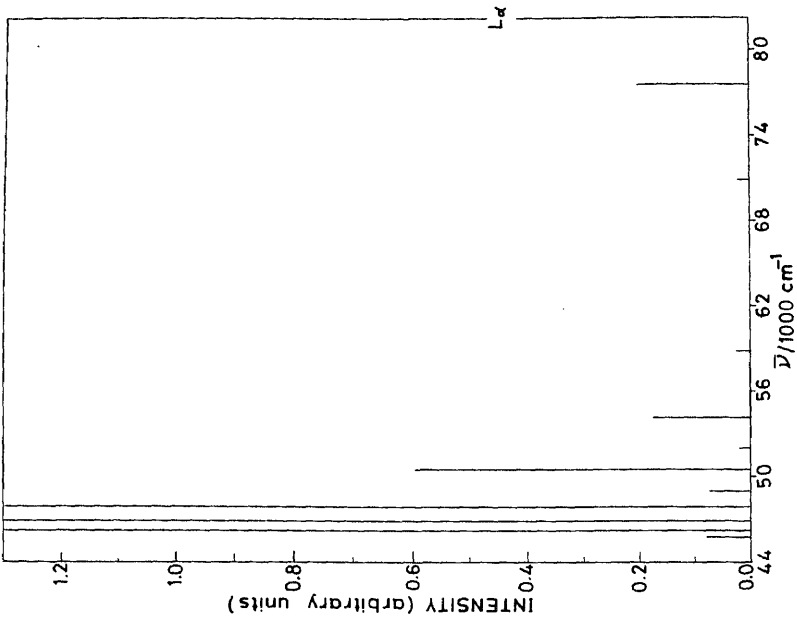
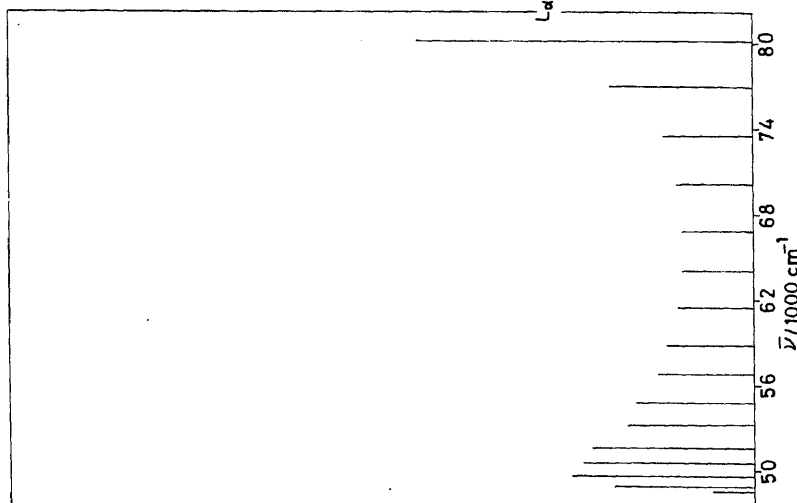


Figure 3. Same as figure 2 for $E = (4/3)V_0 = 0.5333 \text{ eV}$.



Predicted absorption spectrum for $E = V_0/2 = 0.2 \text{ eV}$. L_{α} indicates the Lyman- α

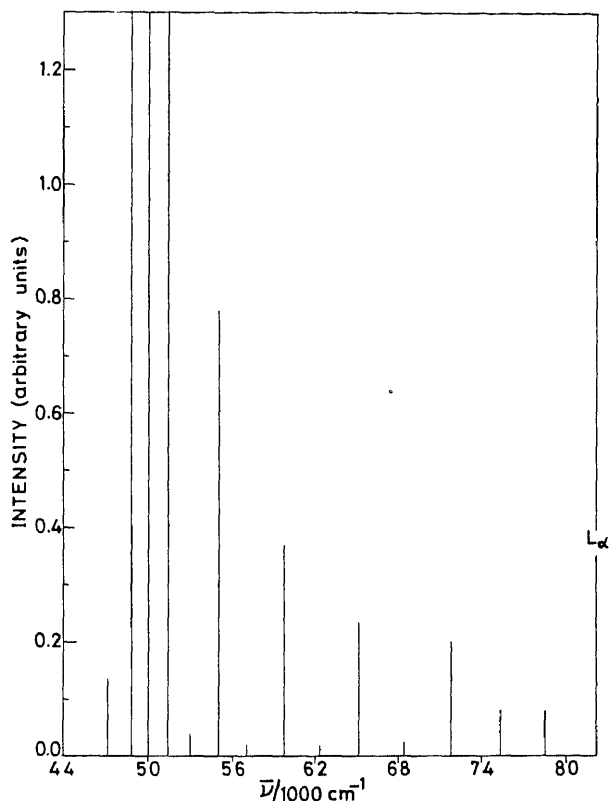


Figure 4. Same as figure 2 for $E = 0.4177$ eV with unit transmission coefficient.

smaller values of the transition frequencies as collision energy is increased. The same basic trend is clearly present in the results of our model calculations in figures 2–4.

Quantitatively, however, there is a basic difference between our results and those of Engel *et al* (1985). Adjacent bound states get farther from each other with increase in E for the rectangular potential well used by us while the spacing between them decreases with increase in energy for an anharmonic (Morse) oscillator used by the other workers (Engel *et al* 1985).

We have tried to rationalize our spectra by studying the $|\psi|^2$ plots of the wave functions in the upper bound states and the ground state. It is clear from the plots in figure 5 that the build-up of probability density for the collision energy below the barrier height is mostly around the classical turning point. Thus the spectral lines corresponding to transitions to the higher bound states of the excited state have greater intensity, because those states have an appreciable value of $|\psi|^2$ around that region of x -space. For collision energies greater than the barrier the transmission coefficient is

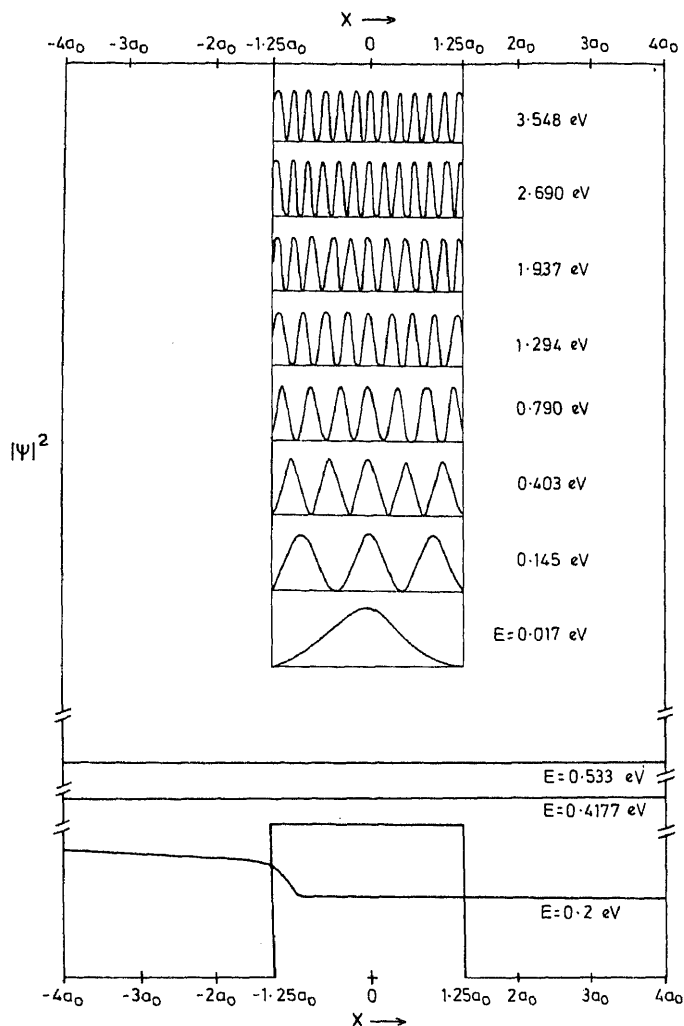


Figure 5. Plots of $|\psi|^2$ for the ground state for different energies and for different bound states of the excited state. For the latter, $|\psi|^2$ is given only for alternate energy states, to avoid crowding.

4. Summary

A model system of a rectangular barrier and a well with parameters appropriate for H_3 , has been considered to study the bound states and scattering states of the system.

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Approximate multiconfiguration variational calculations using partially localized orbitals

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Abstract. A new method is described in which important intra-atomic correlation terms are approximated in a multiconfiguration self-consistent-field (MCSCF) framework without generating large Hamiltonian or Fock matrices. Description in terms of partially localized orbitals (PLO) is preferred over the ordinarily delocalized molecular orbitals (MO). A new approach is also adopted for choosing the virtual excitations as well as for calculating the vector-coupling coefficients.

Keywords. Quantum chemistry; ab-initio theory; multiconfiguration self-consistent field; partially localized orbitals.

Introduction

Recently ab-initio calculations have been carried out by several authors (Goodgame and Goddard 1981; Walch *et al* 1983; Das and Jaffe 1984) to investigate the bonding in transition metal clusters. It was clear from the rather extensive complete active (CAS)SCF calculations by Walch *et al* (1983) that it is necessary to include higher-order correlation effects (such as the intra-atomic correlation) to obtain an adequate description of bonding in these systems. Das and Jaffe (1984) have demonstrated that the inclusion of these higher-order terms within the conventional MCSCF/CI framework (Das and Das 1977) is simplified considerably by going over to representation in terms of what has been called partially localized orbitals (PLO). These are 'Lowdin-normalized' (1980) orbitals that are localized in the sense of Wannier orbitals centered at their individual centres. Using this representation important inter-atomic correlation can be included very efficiently.

General considerations on the importance of nonvalence terms

In the course of our calculations on Cr_2 (Das and Jaffe 1984) we have observed that for accurate wavefunctions beyond the 'valence-only' level, we need to consider only two types of terms involving the virtual orbitals: (a) single excitations representing correlation arising due to readjustment of the orbitals in the charged environment and (b) the double excitations representing the intra-atomic correlation. It is possible to argue that this is generally true for most systems.

In the MCSCF framework, there is an important distinction between the virtual orbitals used for the above two types of excitations. Firstly single excitations of category (a) require one virtual for each valence orbital and hardly ever use a basis space larger

double excitations normally require for their description a much larger basis space. Employment of such a large basis for each atom is impractical even for the smallest molecules. It is, therefore, desirable to find an approximate way of handling these excitations without bringing in anything larger than the molecular basis required at the 'valence-only' level. The work of Goodgame and Goddard (1984) addresses itself to this question by altering the value of some basic electron repulsion integrals such that the constituent atoms have the correct ionization potential and electron affinity. Besides its *ad hoc* nature, such a treatment runs into difficulty for those cases involving more than single charge transfers or those where the inter-shell correlation is important. In what follows we take a more direct route, namely re-express the molecular wavefunction in terms of the various component atomic functions and introduce the intra-atomic correlation in proportion to their relative weights.

Turning to single excitations, the fact that these excitations contribute significantly even if the reference function is optimized has important implications. Let us consider the state of an idealized homopolar system of the symmetry $^1\Sigma_g^+$ described by the following wavefunction:

$$a(1/\sqrt{2})[(d\sigma_A d\pi_A^+)_{s=1} (d\sigma_B d\pi_B^-)_{s=1} + c \cdot c] + (b/2)[(d\sigma_A^2 + d\sigma_B^2)(d\pi_A^+ d\pi_B^- + c \cdot c)]. \quad (1)$$

An MCSCF process will obviously mix in single virtual excitations of the form

$$8^{-1/2} (d\sigma_A^2 + d\sigma_B^2) (d\pi_A'^+ d\pi_B^- + d\pi_A^+ d\pi_B'^- + c \cdot c). \quad (2)$$

The fact that single excitations contribute significantly even after the wavefunction is optimized imply that the contribution is coming through a 'uxu'-type mixing:

$$8^{-1/2} (d\sigma_A^2 - d\sigma_B^2) (d\pi_A'^+ d\pi_B^- - d\pi_A^+ d\pi_B'^- + c \cdot c), \quad (3)$$

which, obviously, cannot be eliminated by a generalized Brillouin's theorem 'process'. This is, in fact, substantiated by the calculations on Cr_2 (Das and Jaffe 1984). One comes to the conclusion that the terms of category (a), in general, must be included even in the MCSCF framework. They can be regarded as truly molecular in the sense that they interact simultaneously with the constituents of the molecule.

On the other hand the intra-atomic correlation excitations remain specific with respect to their respective atoms even in the molecule. This is easily appreciated by considering the hydrogen molecule. If we write the H_2 ($^1\Sigma_g^+$)-wavefunction in terms of localized orbitals as

$$a(s_A^2) + a(s_B^2) + b(s_A s_B), \quad (4)$$

a double excitation such as $s_A^2 \rightarrow \phi_A^2$ mixes significantly only with the first term, while $s_B^2 \rightarrow \phi_B^2$ only with the second. Thus the intra-atomic correlation contribution is easily seen to be given simply by $a^2(\Delta E_A + \Delta E_B)$ to a good approximation, if ΔE is the intra-atomic correlation in H^- . We generalize this approach by assuming that even in the molecular environment the orbitals (MO or PLO) are essentially of LCAO nature:

$$\phi_i = c_{iA} \phi_A + c_{iB} \phi_B.$$

Then it is easy to expand the molecular wavefunction as

$$\Psi = \omega^0 \Phi_A^0 \Phi_B^0 + \omega_{AB}^{(1)} \Phi_A^+ \Phi_B^- + \omega_{BA}^{(1)} \Phi_A^- \Phi_B^+ + \omega_{AB}^{(2)} \Phi_A^{++} \Phi_B^{--} + \omega_{BA}^{(2)} \Phi_A^{--} \Phi_B^{++} + \dots \quad (5)$$

It is easy to see that for a multiple bond rather high orders of ionic states can occur in this expansion. However, unlike the MO-description, PLO will certainly lead to a fast convergence. The corresponding intra-atomic correlation energies are approximated as

$$\Delta E_{\text{corr}} = (\omega^0)^2 [\Delta E_A + \Delta E_B] + (\omega_{AB}^1)^2 [\Delta E_A^+ + \Delta E_B^-] + \dots \quad (6)$$

3. Construction of the approximate MCSCF wavefunction

On the basis of the discussion above we shall consider three types of terms to be treated variationally in different orders of approximation. Firstly, the valence-only terms are treated exactly. The single excitation correlation terms are approximated by first restricting that the virtual orbital used for the promotion of one valence orbital cannot be used for the promotion of another. To simplify the problem of computation of vector-coupling coefficients for the singly excited configurations, the spin-coupling in them is required to be the same as the parent configurations. This is, of course, no real restriction when all the spin-couplings are present in the valence-only wavefunction. Thus for the single excitation $\phi_i \rightarrow \phi_u$, if ϕ_i is singly occupied in the parent configuration, ϕ_u will simply replace ϕ_i with the spin-coupling left intact. If ϕ_i is doubly-occupied, ϕ_i and ϕ_u will be singlet-coupled in the new configuration, all other couplings remaining unaltered. The matrix element between the parent and the resulting configurations is then

$$\langle 0|H|i \rightarrow u \rangle = \sqrt{n_i} \langle i|h|u \rangle + \sqrt{(1/n_i)} \sum_{j \neq i} \langle i|v_{ij}^J J_{jj}^{\text{op}} + v_{ij}^K K_{jj}^{\text{op}}|u \rangle, \quad (7)$$

where n_i is the occupancy of the orbital ϕ_i , v_{ij}^J and v_{ij}^K are the J - and K -vector-coupling coefficients for the diagonal term $\langle 0|H|0 \rangle$ and J_{kl}^{op} and K_{kl}^{op} are the Coulomb and exchange operators:

$$J_{kl}^{\text{op}} \phi_i(\mathbf{r}) = \int \frac{\phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \cdot \phi_i(\mathbf{r})$$

$$K_{kl}^{\text{op}} \phi_i(\mathbf{r}) = \int \frac{\phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \cdot \phi_i(\mathbf{r}) \quad (8)$$

The matrix element between the two excitations $\phi_i \rightarrow \phi_u$ and $\phi_j \rightarrow \phi_v$ is

$$\langle 0; i \rightarrow u | H | 0; j \rightarrow v \rangle = (n_i n_j)^{-1/2} [\langle i | v_{ij}^J J_{vv}^{\text{op}} + v_{ij}^K K_{vv}^{\text{op}} | u \rangle], \quad (9)$$

In the energy expression obtained by considering the above two groups of terms we add the third group, namely the correlation contribution given by (6). This will be our variational energy expression from which to obtain the MCSCF optimization equations, viz. the secular equations for the mixing coefficients and the Fock equations for both the valence and the virtual orbitals (see for example, Das 1981). For the atomic correlation corrections we use the experimental atomic energies along with the scf energies calculated with sufficiently accurate basis. In those cases where no experimental energies are available, it might be necessary to compute the atomic

can, therefore, be written as

$$\begin{aligned}\varepsilon &= A_0^2 \varepsilon_0 + 2A_0 \sum_i B_{ia} A_a \langle a; i \rightarrow u | H | a \rangle \\ &+ \sum_{i,a} B_{ia}^2 \langle a; i \rightarrow u | H | a; i \rightarrow u \rangle,\end{aligned}\quad (10)$$

where

$$\varepsilon_0 = \sum A_a A_b H_{ab},$$

H_{aa} including the intra-atomic correlation correction. We shall assume that the single excitations are small so we need consider them only in the lowest order; that is, we approximate the energy as

$$\begin{aligned}\varepsilon &= \varepsilon_0 + 2 \sum_{i,a} B_{ia} A_a \langle a; i \rightarrow u | H | a \rangle \\ &+ \sum_{i,a} B_{ia}^2 [\langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0].\end{aligned}\quad (11)$$

The optimization of B_{ia} gives

$$B_{ia} = - \frac{A_a \langle a; i \rightarrow u | H | a \rangle}{\langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0}.\quad (12)$$

Thus

$$\varepsilon = \sum A_a A_b H'_{ab},\quad (13)$$

where

$$H'_{ab} = H_{ab} - \delta_{ab} \sum_i \frac{\langle a; i \rightarrow u | H | a \rangle^2}{\langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0}.\quad (14)$$

In order to avoid the destabilization effect of single excitations we optimize the valence orbitals without the orthogonalization constraints with respect to the virtual orbitals. The latter are, however, modified during the optimization process to insure mutual orthogonality. This is done as follows: Let $\mathbf{c}$ be a valence vector and $\mathbf{u}$ a virtual. Considering the variations in these vectors we have

$$\delta\varepsilon = 2(\delta\mathbf{c}^+ \mathbf{F}_c \mathbf{c}) + 2\delta\mathbf{u}^+ \mathbf{F}_u \mathbf{u},\quad (15)$$

where $\mathbf{F}_c$ and $\mathbf{F}_u$ are the Fock operators. While $\mathbf{F}_c$ has, in general, components coming from both ε_0 as well as the single-excitation terms, $\mathbf{F}_u$ has contribution only from the latter. Assuming that only the single excitation $i \equiv (\mathbf{c} \rightarrow \mathbf{u})$ is selected:

$$\mathbf{F}_c \mathbf{c} \equiv \mathbf{F}_{0,c} \mathbf{c} (1 - \sum_a B_{ia}^2) + \sum_a B_{ia} A_a \mathbf{F}_{ia}^0 \mathbf{u} + \sum_a B_{1a}^2 \mathbf{F}_{ia}^d \mathbf{c}\quad (16)$$

$$\mathbf{F}_c \mathbf{u} \equiv - \sum_a B_{ia} A_a \mathbf{F}_{ia}^0 \mathbf{c} + \sum_a B_{ia}^2 \mathbf{F}_{ia}^d \mathbf{u}$$

where $\mathbf{F}_{0,c}$ is the contribution coming from ε_0 and $\mathbf{F}_{ia}^d$, $\mathbf{F}_{ia}^d$ and $\mathbf{F}_{ia}^0$ are the diagonal and off-diagonal contributions from the single excitation terms.

In order that $\mathbf{u}$ stays orthogonal to $\mathbf{c}$ to the first order in $\delta\mathbf{c}$, we must have

$$\delta\mathbf{u} = -(\mathbf{u}^+ \mathbf{S} \delta\mathbf{c}) \mathbf{c}\quad (17)$$

$\mathbf{S}$ being the overlap matrix. Hence

$$\delta\mathbf{u}^+ \mathbf{F}_u \mathbf{u} = -\langle \delta\mathbf{c} | \mathbf{S} \mathbf{u} \rangle \langle \mathbf{F}_u \mathbf{u} | \mathbf{c} \rangle\quad (18)$$

such that

$$\delta\epsilon = \langle \delta\mathbf{c} | [\mathbf{F}_c - |\mathbf{Su}\rangle \langle \mathbf{F}_u\mathbf{u}|] \mathbf{c} \rangle. \quad (19)$$

Thus the Fock equation for $\mathbf{c}$ is

$$(\mathbf{F}_c - |\mathbf{Su}\rangle \langle \mathbf{F}_u|) \mathbf{c} = \sum \lambda_j \mathbf{S} \mathbf{c}_j \quad (20)$$

$\lambda_j\}$ being the Lagrangian multipliers.

1. Matrix elements between the PLO-based configurations

1.1 The vector-coupling problem for dimers

We adopt a new method of calculating the matrix elements where we take advantage of the partitioning of the occupation-space into the fragments *A* and *B*. We use the following theorem (Das 1982): If two spin-symmetrized functions of total spin *s* are formed as products $|s_a \otimes s_b\rangle$ and $|s'_a \otimes s'_b\rangle$ by combining the pairs of fragment spin-functions of spins s_a, s_b and s'_a, s'_b respectively, the matrix elements between these functions can be written as:

$$\begin{aligned} & \langle s'_a \otimes s'_b | H | s_a \otimes s_b \rangle \\ &= C_0 \langle s'_a s'_a, s'_b (-s'_b) | H | s_a s_a, s_b (s'_a - s'_b - s_a) \rangle \\ &+ C_1 \langle s'_a s'_a, s'_b (-s'_b) | H | s_a (s_a - 1), s_b (s'_a - s'_b - s_a + 1) \rangle, \end{aligned} \quad (21)$$

with

$$\begin{aligned} C_0 &= \langle S | s_a s_a, s_b (s'_a - s'_b - s_a) \rangle / \langle S | s'_a s'_a, s'_b (-s'_b) \rangle \\ C_1 &= \langle S | s_a (s_a - 1), s_b (s'_a - s'_b - s_a + 1) \rangle / \langle S | s'_a s'_a, s'_b (-s'_b) \rangle, \end{aligned} \quad (22)$$

where $|sm\rangle$ denotes the spin function with spin *s* and spin-projection *m* and $\langle S | s_1 m_1, s_2 m_2 \rangle$ are the Clebsch-Gordan coefficients.

We note that the matrix element is zero if $|s'_a - s_a| > 1$ or $|s'_b - s_b| > 1$. We consider the four possible cases (all other cases being translatable into one of these):

$$\begin{aligned} & \text{(i) } s'_a = s_a, s'_b = s_b, \text{ (ii) } s'_a = s_a + \xi, s'_b = s_b + \xi, \xi = \frac{1}{2}, 1 \\ & \text{(iii) } s'_a = s_a + \xi, s'_b = s_a - \xi, \xi = \frac{1}{2}, 1 \text{ (iv) } s'_a = s_a, s'_b = s_b + 1 \end{aligned} \quad (23)$$

It is easily shown that except for the diagonal case (i), not more than one '*m*'-component of a fragment function is needed. Also it is necessary to consider the Slater determinants (sp) and their coefficients only for the spin-projections $m = s, s-1$ and $s-2$. We give below the expressions for the matrix elements in each of the above cases:

$$\begin{aligned} & \text{(i) } \langle s_a \otimes s_b | H | s_a \otimes s_b \rangle \\ &= \langle s_a s_a, s_b (-s_b) | H [C_0 [s_a s_a, s_b (-s_b)] + C_1 [s_a s_a - 1, s_b (-s_b + 1)]] \rangle, \\ & \text{(ii) } \langle s_a + \xi \otimes s_b + \xi | H | s_a \otimes s_b \rangle \\ &= C_0 \langle (s_a + \xi) (s_a + \xi), (s_b + \xi) - (s_b + \xi) | H | s_a, s_a, s_b (-s_b) \rangle, \\ & \text{(iii) } \langle s_a + \xi \otimes s_b - \xi | H | s_a \otimes s_b \rangle \\ &= C_0 \langle (s_a + \xi) (s_a + \xi), (s_b - \xi) - (-s_b + \xi) | H | s_a s_a, s_b (-s_b + 2\xi) \rangle, \\ & \text{(iv) } \langle s_a \otimes s_b + 1 | H | s_a \otimes s_b \rangle \\ &= C_1 \langle s_a s_a, (s_b + 1) (-s_b - 1) | H | s_a (s_a - 1), s_b (-s_b) \rangle. \end{aligned} \quad (24)$$

The computation of the vector-coupling coefficients of the matrix elements out in the following steps:

(i) First we form (or take as input) the SD and their coefficients occurring in fragment spin-functions of spin s and projection $m = s$ for all spin-couplings considered in a given calculation:

$$|ts\rangle = \sum_p C_{tp}(nsp)$$

where (nsp) is the p th SD with n open shells and s , the spin-projection and C spin function expansion coefficients.

(ii) The matrix elements that involve only one of the fragments are calculated in a straightforward manner:

$$\langle ts|H|t's\rangle = \sum_{pq} C_{tp} C_{t'q} \langle nsp|H|n'sq\rangle.$$

(iii) For the matrix elements involving both the fragments, we first note that coefficients C_{tp} for $|tm\rangle$ are the same as those for $|t, -m\rangle$. Also in those instances where $|tm\rangle$, $m = s-1, s-2$ are used, the step-down operations are done in an outer loop in order to make the innermost do-loop efficient.

4.2 Extension to multimers

We shall restrict ourselves in this work to what we shall call the fragment correlation (FPC) model in which only those excitations are allowed that connect at most two fragments. While the double excitations are restricted to involve orbitals that belong to no more than two fragments, the single excitations between fragments must not be accompanied by a 'spin-flip'. Thus single excitations such as

$$(\phi_1 \phi_2 \phi_3)_{s_1} (\phi_4 \phi_5 \phi_6)_{s_2} \rightarrow (\phi_2 \phi_3)_{s_1 \pm \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_2 \pm \frac{1}{2}}$$

are allowed but not

$$(\phi_1 \phi_2 \phi_3)_{s_1} (\phi_4 \phi_5 \phi_6)_{s_2} \rightarrow (\phi_2 \phi_3)_{s_1 \pm \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_2 - \frac{1}{2}}$$

or,

$$(\phi_2 \phi_3)_{s_1 - \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_2 + \frac{1}{2}}$$

(the subscripts denoting the values of spins of the fragments).

In this model one can easily derive the following analog of (21) applicable to multimers. If the non-equivalently occupied fragments are 1 and 2 between the two states in question, one can write

$$\begin{aligned} & \langle s'_1 \otimes s'_2 \otimes s_3 \otimes \dots | H | s_1 \otimes s_2 \otimes s_3 \otimes \dots \rangle \\ &= \langle (s'_1 m'_1) (s'_2 m'_2) \dots | H | \sum_{m_1, m_2, \dots} a(m_1 m_2 \dots) (s_1 m_1) (s_2 m_2) \dots \rangle \end{aligned}$$

where all the m -values are the same on both sides, except for 1 and 2, which are $m'_1 + m'_2 = m_1 + m_2$. The coefficients $a(m_1, m_2, \dots)$ are given by

at spin-state is being considered. Thus in the FPC model the evaluation of the elements for multimers follows essentially the same derivation as the dimers.

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Improved Z-dependence of the ground-state energies of neutral atoms

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Abstract. Three *simulated* expressions are suggested regarding the Z-dependence of ground-state energies of neutral atoms at the Hartree-Fock, exact nonrelativistic and relativistic levels. The Hartree-Fock-level $Z^{-1/3}$ -expansion contains three previously derived *plus* two newly derived terms, the latter signifying exchange corrections from the 'inner core' and the 'core mantle' of the Lieb atom. This leads to better agreement than any previous expression, with every coefficient being physically transparent. The Z-dependence of the correlation energy is obtained from a semiempirical Wigner-type correlation potential while the relativistic correction is taken to be in between the values suggested separately by Scott and Schwinger. Agreement with reference values is again better than before. It appears, however, that the atomic $Z^{-1/3}$ -expansion should not proceed beyond terms $O(Z)$.

Keywords. $Z^{-1/3}$ -expansion; atomic binding energy; Thomas-Fermi theory; exchange-correlation energy; single-particle density.

1. Introduction

Based on the Thomas-Fermi (TF) method and its various refinements, the search for a $Z^{-1/3}$ -expansion for the non-relativistic ground-state energies of neutral atoms has been a vintage problem in atomic physics (Dirac 1930; Scott 1952; March 1953, 1957; Ballinger and March 1955; March and Plaskett 1956; Dmitrieva and Plindov 1975; Lieb 1976, 1981; March and Parr 1980; Schwinger 1980, 1981; Shakeshaft *et al* 1981; Shakeshaft and Spruch 1981; Tal and Levy 1981; Aguilera-Navarro *et al* 1982; Bander 1982; Tal and Bartolotti 1982; Conlon 1983). This involves writing the energy as the following function of Z (nuclear charge or the number of electrons)

$$-E(Z) = C_7 Z^{7/3} + C_6 Z^2 + C_5 Z^{5/3} + \dots, \quad (A)$$

where all the C_i 's are, in principle, *known universal numbers arising from well-defined physical effects*. However, the present situation concerning (A) is not quite satisfactory on the basis of *three* criteria: (i) clear physical significance is known only for C_7 , C_6 and C_5 ; (ii) agreement with Hartree-Fock (HF) and nonrelativistic (NR) atomic energies, especially at low Z, is not excellent; and (iii) the length of the above expansion is not known.

There have been two types of studies on (A). The first has tried to calculate C_7 , C_6 and C_5 from first principles (Dirac 1930; Scott 1952; March 1953, 1957; Ballinger and

March 1955; March and Plaskett 1956; Schwinger 1980, 1981; Dmitrieva and Plindov 1975; Lieb 1976, 1981; Bander 1982; Conlon 1983) whereas the second has tried to obtain either C_5 or all three by fitting calculated energies to experimental or *ab initio* energies (Scott 1952; March and Parr 1980; Shakeshaft *et al* 1981; Shakeshaft and Spruch 1981; Tal and Levy 1981; Aguilera-Navarro *et al* 1982; Tal and Bartolotti 1982). The derived values are $C_7 = 0.76874512$ a.u.* (TF value), $C_6 = -0.5$ a.u. [Scott value (1952)] and $C_5 = 0.2699$ a.u. [(Schwinger value (1980))]. With these, the 3-term expansion in (1) reproduces known energy values for $6 \leq Z \leq 80$ at 2% error and at 7% error for the hydrogen atom (Schwinger 1980). If one takes the $Z^{7/3}$ term alone then, in the limit $Z \rightarrow \infty$, this gives the exact NR energy (Lieb 1976; Lieb and Simon 1977), but it overestimates energy badly at low Z with $\approx 30\%$ error (figure 1). On the other hand, workers studying various fitting or interpolation schemes have commented on the presence of oscillatory and/or discontinuity features, depending on the scheme of interpolation.

This paper is an attempt to improve the situation *vis-a-vis* criteria (i)–(iii) above. In §2 we discuss the basis on which two new constants C_4 and C_3 are derived in §3. The results of energy simulation at the HF, NR and relativistic levels are then described in §4, while §5 takes stock of the resulting situation.

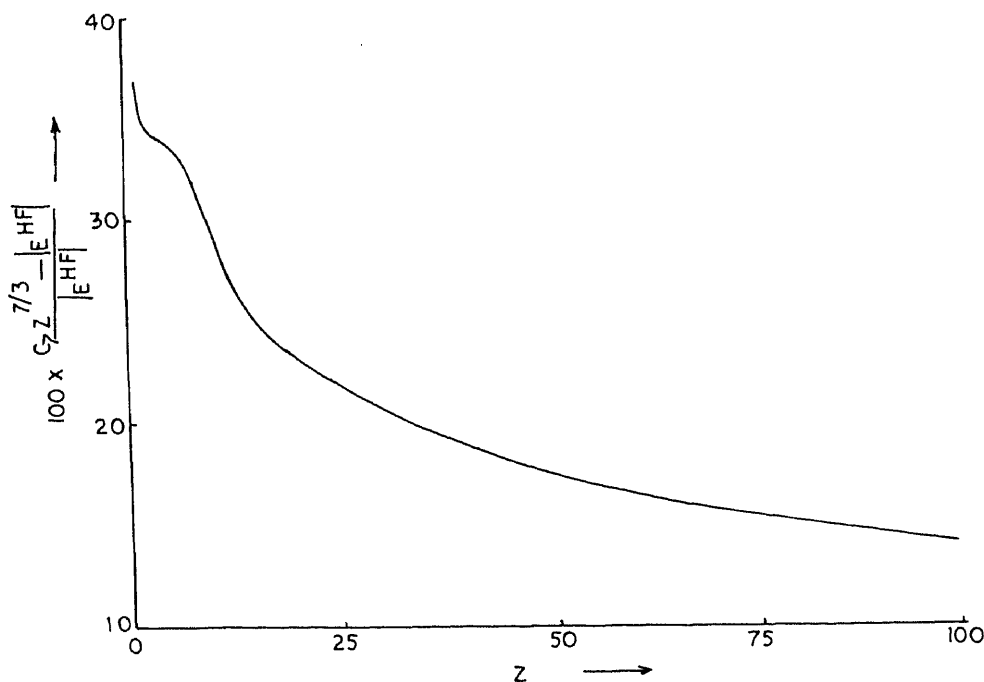


Figure 1. Percent deviation of $C_7 Z^{7/3}$ from atomic ground-state Hartree-Fock energies (Clementi and Roetti 1974; McLean and McLean 1981) as a function of Z .

* Atomic units will be employed throughout this paper.

2. The approach to the problem

The analysis of the present problem requires us to obtain the integral of any local function of the charge density $\rho(\mathbf{r})$ as a function of the nuclear charge Z . This we do below, using an average-density argument. We also utilize Lieb's (1976; 1981) analysis of the Z -dependence of r and ρ in different regions of an atom (in particular, see § Vc of Lieb 1981). Specifically, we consider almost the whole of the atom to consist of an 'inner core', a 'core' and a 'core mantle'. The $Z^{7/3}$ -dependent kinetic energy term arises from the 'core' whereas the Z^2 and $Z^{5/3}$ terms arise from the 'inner core' and 'core mantle' respectively. Similarly, the $Z^{5/3}$ term for exchange energy arises from the 'core', while the 'inner core' and 'core mantle' contribute, respectively, the $Z^{4/3}$ and Z terms. Note that the problem is really open-ended since the $Z^{4/3}$ and Z terms would also contain small kinetic-energy contributions from the region outside the 'core mantle'. However, we feel it is necessary that the included terms correspond to a consistent physical picture and, therefore, we do not consider here the region outside the 'core mantle' (since then, one will also have to consider exchange contributions from this region, and so on again for kinetic energy, etc.).

Let $f(\rho)$ be a local function of $\rho(\mathbf{r})$ and $F[\rho]$ its volume integral. Then the Z -dependence of F is given by

$$\begin{aligned} F &= f(\bar{\rho})V \\ &= f(Z^2/V_0) V_0 Z^{-1}, \end{aligned} \quad (1)$$

where V is the TF volume (Lieb 1976) of a neutral atom with Z electrons, $\bar{\rho} (= Z/V)$ is the average density and the volume V_0 is a universal constant. Writing

$$-E_{TF} = C_k \int \rho^{5/3} d\mathbf{r} = C_7 Z^{7/3} \quad (2)$$

and $V = V_0 Z^\alpha$, one can readily show that $\alpha = -1$ and $V_0 = (C_k/C_7)^{3/2} = 7.218207$ a.u., since $C_k = (3/10)(3\pi^2)^{2/3}$.

Now, in order to find the correction from the 'inner core', consider all the electrons as having been incorporated into a spherical Scott atom (1952) of radius R , where R may extend a little outside the 'inner core' into the 'core'. For this atom, let

$$\rho = Cr^\alpha, \quad (3)$$

where C is a universal constant. The Z -dependence of ρ enters through that of r . The density normalization is

$$4\pi \int_0^R \rho r^2 dr = Z. \quad (4)$$

Taking $Z \sim R^{-1}$ (see Lieb 1981) and using (3), this gives $\alpha = -4$. To obtain C , we equate the Scott (1952) and Weizsäcker energies, viz.,

$$\begin{aligned} \frac{1}{2} Z^2 &= \frac{1}{8} \int \frac{(\nabla \rho)^2}{\rho} d\mathbf{r} \\ &= 2C^{-1/2} \int \rho^{3/2} d\mathbf{r}, \end{aligned} \quad (5)$$

for a spherical atom, using $\rho = Cr^{-4}$. Using (1) and (2) we obtain

$$\rho = 16V_0^{-1}r^{-4}. \quad (6)$$

This gives the radial dependence of electron density in a spherical Scott atom.

Consider now the correction from the 'core mantle'. Here $Z \sim R^{-3}$ (Lieb 1981), where R is the radius of the 'mantled' atom (as before, R may extend a little into the 'core'). Using (3) and (4), we now find $\alpha = -6$, *i.e.*

$$\rho = Cr^{-6}. \quad (7)$$

Replacing $(\nabla\rho)^2$ by $(d\rho/dr)^2$ as well as using (1) and (2), we obtain the Weizsäcker energy for this region as

$$\frac{1}{8} \int \frac{(\nabla\rho)^2}{\rho} d\mathbf{r} = 4.5 Z^{5/3} (CV_0)^{-1/3}. \quad (8)$$

This ought to be identified with the δE_{qu} correction of Schwinger (1980), where

$$\delta E_{qu} = 2 (0.2699) Z^{5/3} / 11. \quad (9)$$

Then

$$\rho = (99/1.0796)^3 V_0^{-1} r^{-6}, \quad (10)$$

which gives the radial dependence of the electron density in the 'core mantle' and in its region of overlap with the 'core'.

Equations (1), (2), (6) and (10) form the backbone of the present work leading to the following results.

3. Simulation of the ground-state energies of neutral atoms at the Hartree-Fock, exact nonrelativistic and relativistic levels

3.1 The Hartree-Fock level

We write the energy as

$$-E_{HF}(Z) = C_7 Z^{7/3} + C_6 Z^2 + C_5 Z^{5/3} + C_4 Z^{4/3} + C_3 Z, \quad (11)$$

where C_7 is the TF value, C_6 is the Scott value and C_5 is the Schwinger value. C_4, C_3 are the exchange corrections to be calculated in view of the fact that the magnitude of the Dirac exchange is less (Shih 1976) than that of the HF exchange.

For a homogeneous electron gas or a gas of slowly varying density, the leading gradient correction to the Dirac exchange is taken as (Kohn and Sham 1965; Shih 1980; Shih *et al* 1980; Gross and Dreizler 1981; Hernandez and Gazquez 1982; Csavinsky and Vosman 1983):

$$K_2[\rho] = \beta \int \frac{(\nabla\rho)^2}{\rho^{4/3}} d\mathbf{r}, \quad (12)$$

where β is given by (Kohn and Sham 1965; Shih 1980; Shih *et al* 1980; Gross and Dreizler 1981; Csavinsky and Vosman 1983):

$$\beta = (-7)/[432\pi(3\pi^2)^{1/3}].$$

Replacing $(\nabla\rho)^2$ by $(d\rho/dr)^2$ for a spherical Scott atom and using (6), we obtain

$$K_2^i[\rho] = 16\beta(16/V_0)^{-1/2} \int \rho^{7/6} d\mathbf{r}. \quad (13)$$

Use of (1) and (2) then gives

$$K_2^i(Z) = 4\beta V_0^{1/3} Z^{4/3}, \quad (14)$$

i.e.

$$C_4 = 0.0129783 \text{ a.u.} \quad (15)$$

Similarly, using (1), (2) and (10) for the 'core mantle', we obtain

$$K_2^m(Z) = 36 \beta Z C^{-1/3}. \quad (16)$$

Hence,

$$C_3 = 0.00126492 \text{ a.u.} \quad (17)$$

Note that both the exchange corrections, C_4 and C_3 , have the same sign as the original $Z^{5/3}$ -exchange term. Thus, at the HF level all the five C_i 's are *derived*, and not *adjusted*, with the physical effects clearly delineated.

3.2 The exact nonrelativistic level

Since both exchange and correlation have a similar origin in interelectronic repulsion, one may think of extending the above picture to cover electron correlation as well. As we shall see below, this does not work, casting doubt on any $Z^{-1/3}$ -expansion for correlation energy.

In the local density approximation, correlation energy is given by

$$E_c[\rho] = \int \varepsilon_c[\rho] \rho \, dr. \quad (18)$$

In order to apply (1) and (2), one must start with a reliable correlation potential $\varepsilon_c[\rho]$. We have examined the parametric forms for $\varepsilon_c[\rho]$ of McWeeny (1976) and Vosko and coworkers (Vosko *et al* 1980; Wilk *et al* 1981) for $0.5 \leq r_s \leq 20$, where $(4/3) \pi r_s^3 = \rho^{-1}$. The values of Vosko and coworkers agree with reference values (Ceperley and Alder 1978, 1980) better than those of McWeeny. However, using Hartree-Fock atomic densities (Clementi and Roetti 1974), we observed that both these correlation potentials overestimate atomic correlation energies, especially at low Z , by 100–250%; such a situation also occurs with Cowan's (1981) statistical prescription for correlation. Therefore, we will employ the Wigner-type parametric formula

$$\varepsilon_c^{\text{at}}[\rho] = -(9.810 + 21.437 \rho^{-1/3})^{-1}, \quad (19)$$

suggested by Brual and Rothstein (1978). As seen in table 1, this gives a much better reproduction of atomic correlation energies (Veillard and Clementi 1968). Using (1) and (2), (19) leads to

$$-E_c^{\text{at}}(Z) = Z[9.810 + 21.437(Z^2/V_0)^{-1/3}]^{-1}. \quad (20)$$

Table 1 lists these values. Comparing columns 2 and 5, we see that the average-density argument via (1) and (2) leads to some overestimation. This is a characteristic feature. Nevertheless, the values from (20) are still better than those from the ε_c 's of McWeeny (1976), Vosko *et al* (1980) and Wilk *et al* (1981).

Thus, the sum of (11) and (20) simulates the exact nonrelativistic energy. Note that (20) contains two adjusted parameters.

Table 1. Calculated values (a.u.) of $-E_c(Z) = -\int \epsilon_c[\rho]\rho dr$, using Hartree-Fock atomic densities⁽ⁱ⁾.

Z	Reference value ⁽ⁱⁱ⁾	Brual-Rothstein value ⁽ⁱⁱⁱ⁾	McWeeny value ^(iv)	Vosko <i>et al</i> value ^(v)	Equation (20)
3	0.0454	0.06472	0.1770	0.1620	0.1010
4	0.0940	0.09163	0.2431	0.2247	0.1525
6	0.1551	0.1593	0.4034	0.3738	0.2684
7	0.1861	0.2044	0.4986	0.4636	0.3313
10	0.381	0.3567	0.7828	0.7464	0.5337
12	0.428	0.4377	0.9119	0.8916	0.6774

⁽ⁱ⁾ Clementi and Roetti 1974; ⁽ⁱⁱ⁾ Veillard and Clementi 1968; ⁽ⁱⁱⁱ⁾ Brual and Rothstein 1978; ^(iv) McWeeny 1976; ^(v) Vosko *et al* 1980; ^(vi) Wilk *et al* 1981.

vanishes giving a finite $E_c[\rho]$. If, like exchange, one expresses $E_c(Z)$ as a sum of $Z^{5/3}$, $Z^{4/3}$ and Z terms, then $\epsilon_c[\rho]$ becomes

$$\epsilon_c[\rho] = A\rho^{1/3} + B\rho^{1/6} + C. \quad (21)$$

If the three parameters A , B and C are now adjusted to reproduce atomic correlation energies (Veillard and Clementi 1968), then the parameters do not have the same sign leading to the unphysical result that $\epsilon_c[\rho]$ vanishes at a nonzero ρ . An identical situation results if one takes any two of the three Z -dependent terms. Further, one should not take $E_c(Z)$ as either a single $Z^{5/3}$, $Z^{4/3}$ or Z term, because this will again lead to an $\epsilon_c[\rho]$ which is not in accord with experience (see (21)). Therefore, it is obvious that if one requires good reproduction of atomic correlation energies, then $E_c(Z)$ should not contain $Z^{5/3}$ to $Z^{1/3}$ terms.

3.3 The relativistic level

For simulation at this level we employ the expression (Scott 1952; Schwinger 1980)

$$-E_{\text{Rel}}(Z) \times 10^6 = C_R Z^{9/2}, \quad (22)$$

where we take $C_R = 3.5$ a.u. This provides better agreement with Dirac-Hartree-Fock values (Desclaux 1973) than the values of 4.0 and 2.4 suggested by Scott (1952) and Schwinger (1980). The $Z^{9/2}$ -term is the leading relativistic correction to the kinetic energy. Note that this is the only parameter adjustment done in this paper.

Thus, the sum of (11), (20) and (22) simulates the relativistic atomic energy. The diminishing relative importance of correlation and increasing importance of relativistic corrections with increasing Z are faithfully mimicked by (20) and (22).

4. Results

Using (11), (20) and (22), we have calculated atomic ground-state energies for $2 \leq Z \leq 110$ and compared them with the appropriate reference values as well as the values of Shakeshaft *et al* (1981) with their median value (0.275) for C_s which includes

correlation. The largest error occurs with $Z = 2$, viz. 3.1 %, 2.8 % and 1.4 % for (11), (20) and (22) respectively. On the whole, the present energies are better than the previous ones, especially at low Z . Table 2 reports values for 10 atoms. A pleasing situation is that for most of the atoms, the simulated HF and nonrelativistic energies lie *above* the corresponding true energies. However, due to parameter adjustment, the physical

Table 2. Comparison of $-E(Z)$ values (a.u.) for neutral atoms with Hartree-Fock, nonrelativistic and relativistic energies.

Z	Hartree-Fock level ⁽ⁱ⁾	Nonrelativistic level ⁽ⁱⁱ⁾	Relativistic level ⁽ⁱⁱⁱ⁾
2	2.86168	2.9037	2.90382
	2.76634	2.7473	2.86175
		2.8220	2.82212
3	7.43272	7.4781	7.4780
	7.22269	7.1946	7.43327
		7.3236	7.32410
4	14.57302	14.6670	14.6685
	14.33280	14.2967	14.5752
		14.4852	14.4870
5	24.52906	24.6530	24.6579
	24.42664	24.3839	24.5350
		24.6352	24.6401
10	128.54705	128.928	129.056
	128.44103	128.385	128.674
		128.975	129.085
15	340.71869	341.240	342.025
	339.19779	339.164	341.420
		340.100	340.786
20	676.75803	—	—
	675.18084	675.202	679.502
		676.477	678.981
40	3538.9172	—	—
	3534.6109	3535.171	3594.81
		3537.607	3594.27
80	18408.984	—	—
	18404.965	18407.963	19623.5
		18411.609	19693.9
90	24359.726	—	—
	24348.155	24352.024	26471.9
		24355.735	26534.2

⁽ⁱ⁾ In this column for every Z , the first number is from Clementi and Roetti (1974) for $2 \leq Z \leq 40$ and from McLean and McLean (1981) for $Z = 80-90$. The second number is from eq. (11).

⁽ⁱⁱ⁾ In this column, for every Z , the first number is from Veillard and Clementi (1968); the second number is from Shakeshaft *et al* (1981), with $C_s = 0.275$; the third number is from the sum of (11) and (20). For $Z > 15$, the first number is not entered.

⁽ⁱⁱⁱ⁾ In this column, for every Z , the first number is the experimental energy (Veillard and Clementi 1968); the second number is the Dirac-Hartree-Fock value (Desclaux 1973); the third number is from the

meaning of the constants in (20) and (22) is not completely clear. Note that the overestimation in energy due to the use of the average-density argument, in converting ρ -dependence into Z -dependence, compensates to a certain extent for the underestimation resulting from C_7 , C_6 and C_5 together.

5. Conclusions

By incorporating the exchange corrections $C_4 Z^{4/3}$ and $C_3 Z$, we have obtained better agreement with HF values than observed before, especially at low Z . Except for the few atoms where the simulated energy has gone below the HF energy, the agreement would improve further if $Z^{4/3}$ - and Z -dependent kinetic-energy contributions are also incorporated. In order to retain physical consistency, we have refrained from doing this. At this level, the physical meanings of all the co-efficients are clear. However, at the NR and relativistic levels this physical clarity is partly lost due to parameter adjustment, although the numerical agreement with reference values improves further. The relativistic situation deserves a first-principles attack.

For practical purposes, if one neglects exchange contributions from outside the 'core mantle', then expansion (A) proceeds only up to $C_3 Z$. We have argued in §3 that the atomic correlation energy should not be expanded in $Z^{-1/3}$, i.e. it should not contain terms from $Z^{5/3}$ to $Z^{1/3}$, if a satisfactory correlation potential and good agreement with atomic correlation energies are desired. It is also worthwhile to note that hardly any work seems to have been done on the Z -dependence of excited states.

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Compton profiles of atoms from electron densities via reciprocal form factors

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Abstract. A new method to extract the Compton profile from the electron density has been proposed. The method is based on the nonlocal density approximation (NLDA) due to Gunnarsson *et al* and Alonso and Girifalco. Initially the reduced first order density matrix has been estimated from the knowledge of the electron density alone through the use of an averaged density distribution, $\bar{\rho}(r)$. The reduced first order density matrix thus obtained has then been employed to extract the reciprocal form factor, $B(r)$. The Compton profile, $J(q)$ may thereby be obtained by a cosine transformation of $B(r)$. These results for the $J(q)$ are in good agreement with their near Hartree-Fock counterparts.

Keywords. Compton profile; reciprocal form factor; electron density; electron momentum density; density matrix.

1. Introduction

The study and measurements of Compton profiles have received a good deal of attention in the past decade or so. The reason for such an interest is that with the advent of intense γ -ray and synchrotron radiation sources very accurate determination of the momentum space properties of electrons in the sample has become possible. Extensive reviews both of theoretical and experimental aspects of Compton scattering and related techniques are available (Williams 1977a, b). The Compton profile is related to the spherically averaged electron momentum density, $\gamma(p)$ via the relation:

$$J(q) = 2\pi \int_{|q|}^{\infty} \gamma(p) p \, dp, \quad (1)$$

where q is the projection of an electron's initial momentum onto the scattering vector. Reciprocally,

$$\gamma(p) = \frac{-1}{2\pi} p^{-1} \left. \frac{dJ(q)}{dq} \right|_{q=p}. \quad (2)$$

Various other properties viz. the $\langle p^n \rangle$ -values may be extracted from the Compton profiles (Benesch and Smith 1973).

$$\langle p^n \rangle = 2(n+1) \int_0^{\infty} J(q) q^n \, dq, \quad 0 \leq n \leq 4, \quad (3)$$

the $\langle p^{-1} \rangle$ is related to the peak height of the Compton profile by

$$\langle p^{-1} \rangle = 2 J(0). \quad (4)$$

However, analysis and interpretation of Compton profiles is not limited to momentum space only. The Fourier transform of the Compton profile viz. the reciprocal form factor, $B(\mathbf{r})$ has been found (Weyrich *et al* 1979) to be a convenient tool to study and interpret simple chemical concepts such as hybridization, and bonding. The spherically averaged $B(r)$ is given by (Thakkar *et al* 1983):

$$B(r) = 2 \int_0^\infty J(q) \cos(qr) dr. \quad (5)$$

The first order reduced density matrix is related to $B(r)$ via the relations (Thakkar *et al* 1983),

$$B(\mathbf{r}) = \int \Gamma(\mathbf{s}/\mathbf{s} + \mathbf{r}) d\mathbf{s}, \quad (6)$$

and

$$B(r) = 1/4\pi \int B(\mathbf{r}) d\Omega. \quad (7)$$

Thus the $B(r)$ function emerges as a convenient bridge between the coordinate and momentum spaces.

The reduced first order density matrices in configuration and momentum space are related to each other by (Benesch and Smith 1973),

$$\Gamma(\mathbf{p}/\mathbf{p}') = [1/(2\pi)^3] \int \Gamma(\mathbf{r}/\mathbf{r}') e^{-i\mathbf{p} \cdot \mathbf{r}} e^{i\mathbf{p}' \cdot \mathbf{r}} d\mathbf{r} d\mathbf{r}'. \quad (8)$$

The electron momentum density, $\gamma(p)$ is the diagonal component of $\Gamma(\mathbf{p}/\mathbf{p}')$ i.e.

$$\gamma(\mathbf{p}) = \Gamma(\mathbf{p}/\mathbf{p}') \quad (9)$$

and the spherically averaged momentum density is given by

$$\gamma(p) = (1/4\pi) \int \gamma(\mathbf{p}) d\Omega. \quad (10)$$

The electron density, $\rho(\mathbf{r})$ may be defined in a similar manner. Unfortunately, the transformation from ρ to γ and the converse is not as yet available contrary to the one between the density matrices as defined by (8). Thus it is necessary to resort to certain approximate procedures to extract momentum density from the electron density and vice versa. The currently available procedures are the ones due to Lam and Platzman (1974), viz., the locally averaged method, (LAM) and Gadre and Pathak (1981), which basically employs semiclassical considerations as those adopted by Burkhardt (1936), Kònya (1949), Coulson and March (1950) (BKCM). Later Pathak *et al* (1983) enforced the constraint of the kinetic energy to the $\gamma(p)$ obtained from the BKCM method. Though there is some improvement in the $\gamma(p)$ predicted, the results are far from acceptable. Recently, Gadre and Chakravorty (1986) proposed leading and tail corrections to the BKCM model. This leads to drastic improvement over some of the momentum space

properties. However, the methods proposed do not yield sufficiently accurate estimates of all properties in momentum space.

In the present work, a new method to determine the Compton profile from the knowledge of electron density alone, is presented. To start with, an approximate reduced first order density matrix in coordinate space is constructed from which the Compton profile is subsequently extracted via the reciprocal form factor.

2. Method

The first order reduced density matrix in coordinate space may be written as (Deb and Ghosh 1983; Ludeña 1983a, b):

$$\Gamma(\mathbf{r}/\mathbf{r}') = \rho^{1/2}(\mathbf{r}) \rho^{1/2}(\mathbf{r}') G(\mathbf{r}, \mathbf{r}'), \quad (11)$$

where $G(\mathbf{r}, \mathbf{r}')$ satisfies the condition,

$$G(\mathbf{r}, \mathbf{r}) = 1. \quad (12)$$

Using an orbital expansion, $G(\mathbf{r}, \mathbf{r}')$ may be written as

$$G^2(\mathbf{r}, \mathbf{r}') = \left[\sum_{i=1}^n \sum_{j=1}^n \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') \phi_j^*(\mathbf{r}) \phi_j(\mathbf{r}') \right] / \left[\sum_{i=1}^n \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \sum_{j=1}^n \phi_j(\mathbf{r}') \phi_j(\mathbf{r}') \right]. \quad (13)$$

Substituting plane waves for ϕ_i 's the homogeneous electron gas pair correlation function is obtained (Deb and Ghosh 1983; Ludeña 1983a, b):

$$G(\mathbf{r}, \mathbf{r}') = 3 j_1(y)/y, \quad (14)$$

where $j_1(y)$ is the first order spherical Bessel function:

$$j_1(y) = [\sin(y) - y \cos(y)]/y^2, \quad (15)$$

with $y = k_F |\mathbf{r} - \mathbf{r}'|$ and k_F = the Fermi momentum.

Another approach to determine an approximate relationship between $\rho(\mathbf{r})$ and the $\Gamma(\mathbf{r}/\mathbf{r}')$ was employed by Gunnarsson *et al* (1976, 1977) and Alonso and Girifalco (1977, 1978). The two particle spinless density matrix, $\Gamma(\mathbf{r}, \mathbf{r}'/\mathbf{r}, \mathbf{r}')$ is given by

$$\Gamma(\mathbf{r}, \mathbf{r}'/\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') - 1/2 \Gamma(\mathbf{r}/\mathbf{r}') \Gamma(\mathbf{r}'/\mathbf{r}), \quad (16)$$

using the relation

$$\Gamma(\mathbf{r}, \mathbf{r}'/\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') [1 + C(\mathbf{r}, \mathbf{r}')]. \quad (17)$$

$C(\mathbf{r}, \mathbf{r}')$ is the correlation factor which is known exactly for a homogeneous electron gas (Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978).

$$C(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \left[\frac{3}{2} \left(\frac{y}{2} \right)^2 - \frac{1}{2} \right] \quad (18)$$

that

$$\rho(\mathbf{r}) = \rho(\mathbf{r}'), \quad (20a)$$

leading to

$$k_f(\mathbf{r}) = [3\pi^2 \rho(\mathbf{r})]^{1/3}. \quad (20b)$$

However, it may be noted that the assumption (20a) is a very drastic one, especially for the atomic and molecular case. This serious defect of the LDA (local density approximation) model necessitated an alternative definition (Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978) of $k_f(\mathbf{r})$ resulting in the non local density approximation (NLDA). This was achieved by rejecting the approximation (20a) and replacing the $\rho(\mathbf{r})$ in (20b) by an average density $\bar{\rho}(\mathbf{r})$ determined by a constraint that the exchange charge density should be conserved (Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978). That means

$$\int \rho(\mathbf{r}) C \bar{\rho}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1; \quad (21)$$

the new correlation factor $C \bar{\rho}(\mathbf{r}, \mathbf{r}')$ is

$$C \bar{\rho}(\mathbf{r}, \mathbf{r}') = (-9/2) [j_1^2(\tilde{y})/\tilde{y}^2], \quad (22)$$

where $\tilde{y} = |\mathbf{r} - \mathbf{r}'| [3\pi^2 \bar{\rho}(\mathbf{r})]^{1/3} = \tilde{k}_f(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|$. Thus $\bar{\rho}(\mathbf{r})$ is determined by solving (21). Another approximation that restores the symmetry of the density matrix is $k_f = [3\pi^2 \rho(|\mathbf{r} - \mathbf{r}'|)]^{1/3}$, which will also be examined.

Thus now with an approximate density matrix being constructed from the electron density, $\rho(\mathbf{r})$ the reciprocal form factor, $B(\mathbf{r})$ may be easily obtained employing (6):

$$\Gamma(\mathbf{r}_1/\mathbf{r}_2) = \rho^{1/2}(\mathbf{r}_1) \rho^{1/2}(\mathbf{r}_2) 3j_1(x)/x, \quad (23)$$

where $x = y = k_f(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2| = [3\pi^2 \rho(\mathbf{r}_1)]^{1/3} |\mathbf{r}_1 - \mathbf{r}_2|$ in the LDA model and $x = \tilde{y} = \tilde{k}_f(\mathbf{r}_1) |\mathbf{r}_1 - \mathbf{r}_2| = [3\pi^2 \bar{\rho}(\mathbf{r}_1)]^{1/3} |\mathbf{r}_1 - \mathbf{r}_2|$ in the NLDA model. In the case of atoms, where $\rho(\mathbf{r}) = \rho(r)$ is a reasonable assumption, the $\Gamma(\mathbf{r}_1/\mathbf{r}_2)$ then simplifies to just a function of r_1, r_2 and $|\mathbf{r}_1 - \mathbf{r}_2| = r$. With this simplification the $B(r)$ as in (6) and (7) may be obtained by a suitable transformation to metric coordinates as utilised by Coulson and Neilson (1961).

$$B(r) = \frac{2\pi}{r} \left\{ \int_0^r \rho^{1/2}(r_1) \frac{3j_1(x)}{x} r_1 dr_1 \int_{r-r_1}^{r+r_1} \rho^{1/2}(r_2) r_2 dr_2 + \right. \\ \left. + \int_r^\infty \rho^{1/2}(r_1) \frac{3j_1(x)}{x} r_1 dr_1 \int_{r_1-r}^{r_1+r} \rho^{1/2}(r_2) r_2 dr_2 \right\} = \frac{2\pi}{r} f(r). \quad (24)$$

Within the NLDA model the determination of $\bar{\rho}(r_1)$ via (21) and (22) remains a cumbersome three-dimensional exercise:

$$1 = (9/2) \int \rho(r_2) j_1^2(\tilde{y})/\tilde{y}^2 d\mathbf{r}_2. \quad (25)$$

Equation (25) can be further simplified by transforming to metric coordinates (Coulson

and Neilson 1961) viz. $r_1, r_2, |\mathbf{r}_1 - \mathbf{r}_2| = r$ yielding

$$1 = \frac{9\pi}{r_1} \left\{ \int_0^{r_1} \rho(r_2) r_2 dr_2 \int_{r_1-r_2}^{r_1+r_2} \frac{j_1^2(\tilde{y})}{\tilde{y}^2} r dr + \int_{r_1}^{\infty} \rho(r_2) r_2 dr_2 \int_{r_2-r_1}^{r_1+r_2} \frac{j_1^2(\tilde{y})}{\tilde{y}^2} r dr \right\}. \quad (26)$$

Now consider the following indefinite integral

$$3 \int \frac{j_1^2(\tilde{y})}{\tilde{y}^2} r dr = 3 \int \frac{j_1^2(\tilde{k}_f r)}{\tilde{k}_f^2 r} dr. \quad (27)$$

Employing recurrence relations (Antosiewicz 1970) and integrating (Gradshteyn and Ryzhik 1980, p. 634) one obtains,

$$3 \int \frac{j_1^2(\tilde{y})}{\tilde{y}^2} r dr = r^2 \left\{ \frac{j_0^2(\tilde{y})}{2} - j_{-1}(\tilde{y}) j_1(\tilde{y}) - \frac{j_1^2(\tilde{y})}{4} - \frac{j_0(\tilde{y}) j_2(\tilde{y})}{3} - \frac{j_2^2(\tilde{y})}{12} \right\} = g(r_1, r). \quad (28)$$

The above solution is an even function of r , thus (26) simplifies after substitution of (28) in (26) to

$$1 = \frac{3\pi}{r_1} \int_0^{\infty} \rho(r_2) r_2 [g(r_1, r)]_{r_1-r_2}^{r_1+r_2} dr_2, \quad (29)$$

where $\tilde{y} = [3\pi^2 \tilde{\rho}(r)]^{1/3} r$. Equation (29) offers a direct method for determination of $\tilde{\rho}$. The above simplification has not been utilised (Deb and Ghosh 1983; Ludeña 1983a, b; Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978) nor pointed out earlier in the literature.

3. Relationships

The $B(r)$ obtained from (24) satisfies certain important conditions. For instance, $B(0) = N$, the number of electrons. This can be verified for (24) employing the differentiation formula for a definite integral [pp. 1098, equation (12.211) of (Gradshteyn and Ryzhik 1980)] and L'Hospital's rule. $B(0)$ is given by

$$B(0) = 2\pi f'(r)|_{r=0} = \int_r^{\infty} \rho^{1/2}(r_1) \frac{3j_1(x)}{x} r_1 dr_1 [\rho^{1/2}(r_1+r) \cdot (r_1+r) + \rho^{1/2}(r_1-r) \cdot (r_1-r)] \quad (30)$$

Thus

Recently Thakkar *et al* (1983) have pointed out that the various momentum space properties could be extracted from the knowledge of $B(r)$ alone. For example, the second moment of the electron momentum density which is twice the kinetic energy is given by

$$\langle p^2 \rangle = -3 \frac{d^2 B(r)}{dr^2} \Big|_{r=0}. \quad (32)$$

The $\langle p^2 \rangle$ -value for the present transformation can be easily determined employing (24) and (32):

$$\langle p^2 \rangle = -6\pi \left[\frac{f''(r)}{r} - \frac{2f'(r)}{r^2} + \frac{2f(r)}{r^3} \right]_{r=0}. \quad (33)$$

Employing L'Hospital's rule one obtains:

$$\langle p^2 \rangle = -2\pi f'''(r)|_{r=0} = \frac{3}{5} \int k_f^2 \rho(r_1) \cdot 4\pi r_1^2 dr_1 + \frac{1}{4} \int \frac{\rho'^2(r)}{\rho(r)} 4\pi r_1^2 dr_1. \quad (34)$$

In the LDA model, (34) with $k_f = [3\pi^2 \rho(r)]^{1/3}$ simplifies to

$$\langle p^2 \rangle = 2(T_0[\rho] + T_w[\rho]). \quad (35)$$

The above solution (35) is identical to the full Thomas-Fermi and Weizsacker components (Murphy 1979). This result is in conformity with the functional forms for kinetic energy for the LDA model (Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978; Deb and Ghosh 1983; Ludeña 1983a, b). The NLDA model, where $k = [3\pi^2 \rho(r_1)]^{1/3}$ for which the $\langle p^2 \rangle$ -value is:

$$\langle p^2 \rangle = 2 \left\{ T_w[\rho] + \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{2/3}(r_1) \rho(r_1) 4\pi r_1^2 dr \right\}. \quad (36)$$

Another approximation, viz., $k_f = [3\pi^2 \rho(|\mathbf{r}_1 - \mathbf{r}_2|)]$ was also tried out which leads to a gross overestimate of the $\langle p^2 \rangle$ -value

$$\langle p^2 \rangle = 2 \left\{ T_w[\rho] + \frac{3}{10} (3\pi^2)^{2/3} \rho^{2/3}(0) N \right\}. \quad (37)$$

In the LDA model, the full Thomas-Fermi and Weizsacker contributions to kinetic energy are unacceptable features. As is known from numerous numerical and theoretical studies (Murphy 1979), the total kinetic energy may be represented fully by one term (e.g. T_0) and a fraction of the other one (e.g. $1/9 T_w$) as the correction term. However, from these analyses, the NLDA model seems to yield a much more reasonable value for the kinetic energy (Gunnarsson *et al* 1976, 1977; Alonso and Girifalco 1977, 1978; Deb and Ghosh 1983; Ludeña 1983a, b).

In the next section the results for the Compton profile, $J(q)$ for the nitrogen and argon atoms employing the NLDA model are presented.

contrary to Deb and Ghosh (1983), where $\bar{\rho}(r)/(\rho(r))$ was determined to be zero numerically at $r = 0$. This can be easily verified from (25). For atoms with two electrons, $\bar{\rho}(r) = 0$ for all r is a particular solution in which case

$$\Gamma(\mathbf{r}/\mathbf{r}') = \rho^{1/2}(\mathbf{r})\rho^{1/2}(\mathbf{r}'), \quad (38)$$

and employing (8)

$$\gamma(\mathbf{p}) = (FT\rho^{1/2})^2. \quad (39)$$

The $B(r)$ was computed from (24) and then the Compton profile was extracted via the relation

$$J(q) = \frac{1}{\pi} \int B(r) \cos(qr) dr. \quad (40)$$

The results for $J(q)$ for nitrogen and argon atoms are presented in table 1. It may be seen that the overall prediction of $J(q)$ is indeed a good one. The $J(0)$ value which is numerically equal to half the $\langle p^{-1} \rangle$ -value seems to be estimated extremely well, the typical relative percent error being less than one percent.

5. Concluding remarks

The present work reports for the first time a reasonably accurate method for extracting atomic Compton profiles exclusively from the knowledge of electron density. This vital link is established via the reciprocal form factor. Also, a better and a more direct

Table 1. A comparison of Compton profiles for nitrogen and argon atoms employing the NLDA model and the NHF wavefunctions (all values are in Hartree atomic units).

q	Nitrogen		Argon	
	NLDA ^{a,b}	NHF ^c	NLDA ^{a,b}	NHF ^c
0	2.7560	2.7986	5.0468	5.0635
0.05486	2.7471	2.7910	5.0325	5.0563
0.13960	2.6990	2.7498	4.9557	5.0156
0.21672	2.6223	2.6819	4.8336	4.9438
0.57765	2.0169	2.0615	3.8758	4.1092
0.92748	1.3949	1.3372	2.8809	2.8925
1.4672	0.7847	0.6430	1.9015	1.5935
2.2768	0.3236	0.2953	1.0751	0.9516
6.0657	0.0261	0.0450	0.2390	0.2433

^a The electron density $\rho(r)$ was computed from Near Hartree Fock wavefunctions (NHF) of Clementi E and Roetti C (1974) *At. Data and Nucl. Data Tables* **14** 177.

^b The present work employing the non local density approximation. See text for details.

^c The $J(q)$ for the NHF framework was extracted via direct Fourier transformation of wave functions.

method for determination of $\bar{\rho}(r)$ is made possible with an assumption of spherical symmetry of $\rho(r)$ for atoms.

The present procedure is unsurpassed in accuracy in estimation of the Compton profiles by all currently known methods viz. the BKCM, Lam and Platzman 1974, and Gadre and Chakravorty (1986) procedures. The present work is particularly relevant in the light of recent developments in the density functional theory (see for example, Bamzai and Deb 1981; Parr 1983) since an explicit transformation between ρ and γ is as yet unknown. An extension to molecules (Pathak *et al* 1984) would be interesting though far from straightforward.

Thus, the reciprocal form factor provides an useful connection between electron density and Compton profile for atoms.

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Sum rules in inelastic gas-surface scattering

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Abstract. An explanation for sum-rules observed in gas-surface scattering is offered via a classical scaling theory for inelastic collisions.

Keywords. Classical scaling principles; sum rules; factorizations in molecular scattering.

1. Introduction

A series of elegant experiments have been carried out recently by Janda and co-workers (Janda *et al* 1980, 1983; Hurst *et al* 1983) on the scattering of supersonic monoenergetic beams from clean metal surfaces. One result from these studies is that the average final kinetic energy of the scattered particle, $\langle E_f \rangle$, depends on the average initial kinetic energy, $\langle E_i \rangle$, and the surface temperature, T_s , via a simple linear relationship,

$$\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_s), \quad (1)$$

where the coefficients α_g, α_s depend only on the scattering angle, and k_B is the Boltzmann constant. A number of theoretical models (Baker and Auerbach 1979; Grimmelman *et al* 1980; Levine and Silbey 1981) have offered an explanation of the above result, which has since been seen to hold in a model semiclassical study of gas-surface scattering as well (Agarwal and Raff 1982).

The purpose here is to point out that an equation such as (1), termed a sum-rule (Levine and Silbey 1981), derives from a recently formulated classical scaling theory (DePristo 1981; Ramaswamy 1984a) for inelastic processes. The scaling approach, described below, offers a novel viewpoint of the inelastic scattering process, and permits a different interpretation of the experimental results (see also Richard and DePristo 1983).

2. Scaling theory

For convenience we consider a coplanar scattering geometry, for which the total Hamiltonian is given as

$$H = H_g + H_s + V(\mathbf{x}, \mathbf{R}). \quad (2)$$

The origin of the coordinate system (see, for example, Goodman 1975; Bernasek and

merely the kinetic energy, $H_g = p_R^2/2m$, with m the atomic mass. p_R is the momentum conjugate to the coordinate R , which describes the position of the gas particle relative to the origin. (We will confine our attention to this simple case). The surface Hamiltonian can be expressed in terms of normal-mode coordinates (Kittel 1971; Goldstein 1980):

$$H = \sum_k (\dot{x}_k^2 + \omega_k^2 x_k^2)/2, \quad (3)$$

where k indexes the normal modes of frequency ω_k . For a given experimental configuration (Janda *et al* 1980, 1983; Hurst *et al* 1983), the angle of incidence, θ_i , is fixed. At the beginning of the collision, the interaction potential $V \rightarrow 0$ (at $t = t_0$, $R = R^0 \rightarrow \infty$), and then H_g and H_s are individually constants of the motion. We transform to an action-angle representation (Goldstein 1980) at $t = t_0$: the actions are the constants of motion. Thus

$$H_s \rightarrow \sum_k \omega_k J_k / 2\pi = \sum_k \omega_k (n_k + 1/2) \hbar \quad (4)$$

where J_k are the surface action variables (or alternatively, the n_k are the phonon occupancies). The angle variables conjugate to these actions are ω_k . Similarly, the 'parallel' and 'perpendicular' components of the momentum of the gas particle are action variables as well, $\mathcal{J}_1 = p_{\perp}$, and $\mathcal{J}_2 = p_{\parallel}$, with conjugate angle variables ϕ_1 and ϕ_2 .

Within a classical scenario, the gas-solid collision is simulated by an ensemble of trajectories. For every trajectory, the initial kinetic energy is fixed, $E = [(\mathcal{J}_1^0)^2 + (\mathcal{J}_2^0)^2]/2m$. The initial orientation is fixed at θ_i . ϕ_1^0, ϕ_2^0 are fixed so that R^0 is some large value and $V(\mathbf{x}, \mathbf{R}) \rightarrow 0$. The value of all variables at $t = t_0$ is indicated by superscript 0. The phonon occupancies (Kittel 1971) are related to the surface temperature (in the high temperature approximation) through (Kittel 1971)

$$(n_k + 1/2) = [\exp(\hbar \omega_k / k_B T_s) - 1]^{-1} \approx k_B T_s / (\hbar \omega_k), \quad (5)$$

which fixes the initial surface actions J_k^0 . What differ from trajectory to trajectory are the surface angle variables, $\mathbf{w}^0$. This leads to a distribution in the scattering angle θ_f , and the final kinetic energy E_f .

Since the measurement is carried out at a specific scattering angle, this corresponds to sampling only a specific set of initial surface-angles, $\mathbf{w}^0$. We are interested in determining the variation in the final kinetic energy with changing initial conditions. The equation of motion for the kinetic energy of the gas, H_g , is (Ramaswamy 1984a)

$$dH_g/dt = -\{H, H_g\} = -\{V, H_g\} = L_v(t)H_g; \quad (6)$$

$\{, \}$ is the Poisson bracket. Equation (6) can be solved implicitly to yield

$$H_g(t = \infty) - H_g(t_0) = E_f - E_i = G(\{V\}; \mathbf{J}^0, \mathbf{w}^0; \mathcal{J}^0, \phi^0), \quad (7)$$

where

Note that the RHS of (8) is evaluated at the *initial* values of all variables. For a particular scattering angle, θ_f , the RHS can be expanded in a Taylor series in the initial action variables to yield

$$E_f - E_i = G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0) + \sum_{l=1}^2 \frac{\partial G}{\partial \mathcal{J}_l^0} \mathcal{J}_l^0 + \sum_{k=1} \frac{\partial G}{\partial J_k^0} J_k^0 + \dots \quad (9)$$

$$= G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0) + 2 \frac{\partial G}{\partial E_i} E_i + (2k_B T_s) \sum_k \frac{1}{\hbar \omega_k} \frac{\partial G}{\partial J_k^0} + \dots$$

$$= \bar{\alpha}_0 + \bar{\alpha}_g E_i + \bar{\alpha}_s 2k_B T_s, \quad (10)$$

with

$$\bar{\alpha}_0 = G(\{V\}; \mathbf{0}, \mathbf{w}^0; \mathbf{0}, \phi^0), \quad (11a)$$

$$\bar{\alpha}_g = 2(\partial G / \partial E_i), \quad (11b)$$

$$\bar{\alpha}_s = \sum_k (\partial G / \partial J_k^0) / \omega_k. \quad (11c)$$

This analysis yields explicit expressions for the coefficients $\bar{\alpha}$ [through (8) and (11)], and it is clear that these are independent of the surface temperature or the incident kinetic energy, but depend on the scattering angle. Further, taking the limit $T_s \rightarrow 0$, $E_i \rightarrow 0$, it can be seen that $\bar{\alpha}_0 = 0$. Taking these limits separately yields $\bar{\alpha}_g < 0$, $\bar{\alpha}_s > 0$. These observations are in accord with experimental results (Janda *et al* 1983; Hurst *et al* 1983). Since the scaling form holds (DePristo 1981; Ramaswamy 1984a) for each initial kinetic energy at fixed T_s , the proper relationship for average energies, (1), is regained.

It must be noted that (10) is in principle (DePristo 1981; Ramaswamy 1984a) an infinite expansion in the initial constants of the motion—here E_i and T_s . It is an *empirical* observation (Agrawal and Raff 1982; Janda *et al* 1980, 1983; Hurst *et al* 1983) that for gas-metal inelastic scattering the higher order terms are negligible. One can therefore expect departures from this simple behaviour when the conditions for the validity of the linear scaling approximation are not satisfied.

3. Discussion

The applicability of the scaling in the present context suggests some interesting extensions. For a molecular gas incident on a surface, H_g will include an internal molecular Hamiltonian in (2). Then the Taylor series expansion in (9) will involve the actions (or quantum numbers) corresponding to the internal degrees of freedom as well. The scaling law that obtains then is similar to (10), with additional terms in the *initial* quantum numbers of the gas molecule,

$$\langle E_f \rangle = \alpha_g \langle E_i \rangle + \alpha_s (2k_B T_s) + \beta_1 N + \beta_2 N^2 + \dots, \quad (12)$$

or at fixed E_i and T_s ,

$$\langle E_f \rangle = \beta_0 + \beta_1 N + \beta_2 N^2 + \dots, \quad (13)$$

which is the usual form of the scaling law in atom-molecule collisions (Ramaswamy and

molecule, and the quantum number is denoted by N). It would be of interest to determine whether such behaviour is indeed followed in an initial state-selected experiment. In another context, we have shown (Ramaswamy 1984b; Ramaswamy and Bhargava 1984; Bhargava and Ramaswamy 1985) that the scaling coefficients can be given precise quantum-mechanical meaning, since they are related to quantum transition probabilities. A full scaling analysis would thus make possible the interpretation of empirical coefficients, such as appear in (1), (12) or (13), in terms of inelastic state-to-state quantities.

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***Ab initio* calculations on lithium-bonded dimers: a brief review**

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Abstract. *Ab initio* calculations on a number of lithium-bonded dimers are reviewed and the properties of lithium bonds vis-a-vis that of hydrogen bonds are discussed.

Keywords. *Ab initio* calculations; lithium-bonded dimers; three-centre interaction.

1. Introduction

Association between molecules containing polar HX bonds and nonbonding electron pairs is characterised by relatively high energies of interaction and unique geometries. This type of molecular interaction is generally attributed to hydrogen bonding. Hydrogen is, however, not unique in its ability to participate in a three-centre interaction. There have been speculations (Shigorin 1959; West and Glaze 1961; Brown *et al* 1962) over the years that lithium being a congener of hydrogen might also be involved in a similar type of interaction giving rise to lithium-bonding.

Ault and Pimental (1975) were the first to provide experimental proof for the existence of a Li-bond in $\text{H}_3\text{N} \dots \text{LiX}$ ($X = \text{Cl}, \text{Br}$) complexes. They found the frequency shifts of the Li-X stretching bands in these complexes qualitatively similar to those observed for analogous proton donors. However, these frequency shifts were considerably smaller than in the corresponding H-bonded complexes and the IR intensity changes characteristic of H-bonds were absent. Later on, Ault (1978) carried out matrix isolation IR spectroscopic studies on the 1:1 complexes of ammonia and water with a number of alkali halides.

Despite the recognition of Li-bonding as an important type of three-centre interaction, the amount of experimental work done to date on Li-bonded complexes has been rather meagre. Thus most of our current knowledge concerning Li-bonding has been derived from theoretical work done in this field. Kollman *et al* (1970) were the first to theoretically investigate the properties of the Li-bond by means of *ab initio* SCF calculations. Since then a number of *ab initio* (Kollman *et al* 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976; Szczesniak *et al* 1976; Szczesniak and Ratajczak 1977, 1980; Umeyama and Morokuma 1977; Kulkarni and Rao 1983; Latajka and Scheiner 1984) and semiempirical (Szczesniak *et al* 1976; Latajka *et al* 1977) calculations have been reported on a variety of Li-bonded dimers. Barring a few (Kollman *et al* 1972; Latajka and Scheiner 1984), these calculations have mostly been carried out at the SCF level. We have in the present article reviewed the results of *ab initio* calculations on a number of Li-bonded dimers in an attempt to elucidate the essential features of Li-

bonding. We have confined our attention only to dimers since to the best of our knowledge no *ab initio* calculation has yet appeared on larger systems.

The results of the *ab initio* calculations are presented and analysed in the next section which is followed by a discussion of the properties of Li-bonds vis-a-vis that of H-bonds. Some remarks concerning Na-bonds have been made in the concluding section of the article.

2. Results of *ab initio* calculations on some Li-bonded dimers

The predicted geometry and dimerisation energy* of the Li-bonded dimers, namely, $(\text{LiH})_2$ (linear and cyclic), $(\text{LiF})_2$ (linear and cyclic), HLiF_2 (linear and cyclic), $\text{H}_3\text{N} \dots \text{LiX}$ ($X = \text{H, F, Cl}$), $\text{H}_2\text{O} \dots \text{LiX}$ ($X = \text{F, Cl}$), $\text{CH}_3\text{OH} \dots \text{LiX}$ ($X = \text{F, Cl}$), $\text{C}_2\text{H}_4 \dots \text{LiX}$ ($X = \text{H, F}$) and $\text{C}_2\text{H}_2 \dots \text{LiH}$ are summarised in table 1. All these results refer to *ab initio* SCF calculations. We shall first discuss the results of calculations on individual or closely related systems and then attempt to generalise them as far as possible.

The complexes, $(\text{LiH})_2$, $(\text{LiF})_2$ and LiHF_2 have been investigated (Kollman *et al* 1970, 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976) both in linear and cyclic forms. The linear form of $(\text{LiH})_2$ is found to be asymmetric ($C_{\infty v}$)—the LiH bond of one monomer is contracted and that of the other is elongated upon complex formation. Two sets of calculations (Kollman *et al* 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976) which have been performed using different basis sets yield almost identical results. The cyclic (D_{2h}) form of $(\text{LiH})_2$ is found to be more stable than the linear one by about 21 kcal/mol. This extra stability is due to the formation of an additional Li-bond in the cyclic form. In this form the LiH distance is stretched by a much wider margin (0.16 Å) and the HH distance is substantially longer than the LiLi distance. The latter structural feature is attributed (Kollman *et al* 1972) to the fact that the HOMO (b_{2u}) of cyclic $(\text{LiH})_2$ has a node between the hydrogens and none between the lithiums. Configuration interaction (CI) calculations including all single and double excitations from the valence MO were carried out (Kollman *et al* 1972) for this system at its SCF—computed geometry. These results indicate that electron correlation has negligible effect on the dimerisation energy of $(\text{LiH})_2$.

Both the linear and the cyclic (D_{2h}) forms of $(\text{LiF})_2$ are far more stable than the corresponding form of $(\text{LiH})_2$. Moreover, like $(\text{LiH})_2$ the cyclic form of $(\text{LiF})_2$ has much higher dimerisation energy than the linear form. Inclusion of *p* orbitals on lithium decreases the LiF distance and the dimerisation energy, and increases the LiLi distance in the linear form of $(\text{LiF})_2$. When *d* orbitals on fluorine are included (Baskin *et al* 1973) the dimerisation energy is further reduced. It may be noted that the LiF distances of the monomers have been kept fixed while optimising the geometry of linear $(\text{LiF})_2$. Had these distances also been optimised, one could probably have found the asymmetric form to be more stable than the symmetric one as in the case of $(\text{LiH})_2$. The structural features of cyclic $(\text{LiF})_2$ are quite similar to those of cyclic $(\text{LiH})_2$ —the LiF distance is considerably elongated (by 0.16 Å) and the FF distance is longer than the

* For systems containing only one dicoordinated Li atom, the dimerisation energy is equal to the Li-bond energy while for systems containing two such Li atoms the dimerisation energy is twice the Li-bond energy.

Table 1. Equilibrium geometry and dimerisation energy (DE) of some lithium-bonded dimers.

Dimer	Structure ⁽ⁱ⁾	Geometry ⁽ⁱⁱ⁾	Δr (Å)	DE (kcal/mol)	Basis set	Reference
(LiH) ₂	1a	$R = 3.44, r_1 = 1.63$ $r_2 = 1.68$	$\Delta r_1 = -0.01$ $\Delta r_2 = 0.04$	25.11	Li(10s, 2p) H(8s, 1p)	Rychlewski and Sabin (1976)
(LiH) ₂	1a	$R = 3.45, r_1 = 1.62$ $r_2 = 1.67$	$\Delta r_1 = -0.01$ $\Delta r_2 = 0.04$	25.98	Li(9s, 5p/4s, 2p) H(5s, 2p/2s, 1p)	Kollman <i>et al</i> (1972)
(LiH) ₂	1b	$r_1 = 2.36$ $r_2 = 2.73$ $r_3 = 1.80$	$\Delta r_3 = 0.16$	47.2	Li(9s, 5p/4s, 2p) H(5s, 2p/2s, 1p)	Kollman <i>et al</i> (1972)
(LiF) ₂	1a	$R = 3.38/3.43$ ⁽ⁱⁱⁱ⁾ $r = 1.667/1.587$	(iv)	56.3/ 46.0	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p)	Kollman <i>et al</i> (1970)
(LiF) ₂	1a	$R = 3.36,$ $r = 1.56$	(iv)	36.4	Li(9s, 3p/4s, 2p) F(9s, 5p, 2d/4s, 2p, 1d)	Baskin <i>et al</i> (1973)
(LiF) ₂	1b	$r_1 = 2.22$ $r_2 = 2.65$ $r_3 = 1.72$	$\Delta r_3 = 0.16$	66.7	Li(9s, 3p/4s, 2p) F(9s, 5p, 2d/4s, 2p, 1d)	Baskin <i>et al</i> (1973)
HFLiF	1c	$R = 3.567/3.567$ ⁽ⁱⁱⁱ⁾ $r = 1.672/1.592$ $r' = 0.916$	$\Delta r = 0.005/0.004$	13.5/ 16.2	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p) H(5s/1s)	Kollman <i>et al</i> (1970)
HFLiF	1d	$R = 2.60$ $\theta_H = 45,$ $\theta_{Li} = 60$ $r = 1.667$ $r' = 0.916$	(iv)	15.1	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p) H(5s/1s)	Kollman <i>et al</i> (1970)
H ₃ N-LiH	1e	$R = 2.05/2.05$ NH ₃ ^(v)	$\Delta r = 0.02/-$	23.01/-	vdz/dzp ^(vi)	Szczesniak and Ratajczak (1980)
H ₃ N-LiF	1e	$R = 2.02,$ $r = 1.634$ NH ₃ ^(vii)	$\Delta r = 0.02$	28.65	N and F(10s, 5p) Li(10s) H(5s)	Szczesniak <i>et al</i> (1976)

Table 1. (Continued)

Dimer	Structure ^(a)	Geometry ^(a)	Δr (Å)	Δr (Å)	Basic set	Reference
H_3N-LiF	1c	$R = 2.05$ $r = 1.603$ $NH_3^{(m)}$		25.31	N and F(10s 5p) Li(10s)	Szostek and Ratajczak (1977)
H_3N-LiF	1c	$R = 2.07$ 2.073 ^(m) $r = 1.582$ 1.592 NH_3 geometry ^(m)	$\Delta r = 0.018$ 0.014	22.89(S) Si ^(a) 22.81(M) Si ^(a) 23.46(S) M ^(a) 23.52(M) M ^(a) for NH_3	6-31G** (2d) for LiF 6-31G** (1p 2d) for NH_3	Latajka and Schermer (1984)
H_3N-LiF	1c	$R = 1.951$ $r = 1.420$ $\angle HNLi = 112.6$ $\angle HNH = 106.1$ NH_3 geometry ^(m)	$\Delta r = 0.013$	47.53	STO-3G	Kulkarni and Rao (1983)
$H_3N-LiCl$	1c	$R = 1.936$ $r = 1.955$ $\angle HNLi = 112.8$ $\angle HNH = 105.9$ NH_3 geometry ^(m)	$\Delta r = 0.022$	54.3	STO-3G	Kulkarni and Rao (1983)
$H_3N-LiCl$	1c	$R = 2.036$ $r = 2.082$ NH_3 geometry ^(a)	$\Delta r = 0.015$	25.46(S) Si ^(a) 26.05(S) M ^(a)	6-31G** (2d) for LiCl 6-31G** (1p 2d) for NH_3	Latajka and Schermer (1984)
H_3O-LiF	1f	$R = 1.774$ $r = 1.423$ $\angle HOLi = 126.8$ $\angle HOH = 104.6$ H_2O geometry ^(m)	$\Delta r = 0.016$	48.34	STO-3G	Kulkarni and Rao (1983)
$H_3O-LiCl$	1f	$R = 1.744$ $r = 1.954$ $\angle HOLi = 126.5$ $\angle HOH = 105.5$ H_2O geometry ^(m)	$\Delta r = 0.021$	55.23	STO-3G	Kulkarni and Rao (1983)

Chemical Compound	Reference	Δr	STO-3G	Author
CH_3OHLiCl	1f	$\Delta r = 0.018$	52-12	Kulkarni and Rao (1983)
$\angle \text{HOC} = 104.1$ $\text{CH}_3\text{OH geometry}^{(\text{xiii})}$ $R = 1.776$, $r = 1.951$ $\angle \text{COLi} = 115$ $\angle \text{HOC} = 104.1$				
$\text{C}_2\text{H}_2\text{LiH}$	1g	$\Delta r = 0.0/-$	8-14/8-93	Szczesniak and Ratajczak (1980)
$\text{C}_2\text{H}_4\text{LiH}$	1h	$\Delta r = 0.0$	8-67	Szczesniak and Ratajczak (1980)
$\text{C}_2\text{H}_4\text{LiF}$	1h	$\Delta r = 0.0$	8-75	Szczesniak and Ratajczak (1977)

(6) For structure see figure 1; (i) bond length in Å and angles in degrees; (ii) without $p/\text{with } p$; (iii) fixed monomer geometry; (iv) geometry of NH_3 taken from Herzberg (1950); (v) $\text{O}=\text{P}=\text{O}$ double bond length + polarisation; (vi) geometry of NH_3 taken from Snyder and Bash (1972); (vii) SCF geometry/MP2 geometry; (viii) $\text{N}=\text{S}=\text{C}$, $\text{M}=\text{MP}2$; (ix) $\text{S}=\text{C}=\text{S}$ SCF geometry/MP2 calculation; (x) $\text{r}(\text{NH})=1.011 \text{ Å}$, $\angle \text{HNH}=107.6^\circ$; (xi) $\text{r}(\text{NH})=1.03 \text{ Å}$, $\angle \text{HNH}$ geometry; (xii) $\text{r}(\text{OH})=0.989 \text{ Å}$, $\angle \text{HOH}=100.0^\circ$; (xiii) $\text{r}(\text{OH})=1.007 \text{ Å}$, $\angle \text{HOH}=100.0^\circ$; (xiv) $\text{r}(\text{OH})=1.03 \text{ Å}$, $\angle \text{HOH}=103.0^\circ$; (xv) geometry of NH_3 taken from Fisher-Hjalmar and Siegbahn (1973).

LiLi distance. The predicted dimerisation energy of $(\text{LiF})_2$ is in good agreement with experiment (Kusch 1958).

The mixed dimer of HF and LiF can exist either in the H-bonded form, $\text{Li-F} \dots \text{H-F}$ or in the Li-bonded $\text{H-F} \dots \text{Li-F}$ in the linear configuration. In table 1 we have included the results of calculations on the Li-bonded form only. It has been predicted (Kollman *et al* 1970) to be less stable than the H-bonded form. The cyclic dimer contains one Li-bond and one H-bond. Since the latter is considerably weakened due to the loss of linearity in the structure, the dimerisation energy of the cyclic form is only slightly higher than that of the linear Li-bonded form. In contrast to $\text{LiF} \dots \text{LiF}$, inclusion of Li p orbitals in the basis set has only a marginal effect on the Li-bond energy in $\text{HF} \dots \text{LiF}$. The stretching of the LiF distance in this complex is negligible.

The Li-bond energy in the $A \dots \text{LiX}$ ($A = \text{NH}_3$; $X = \text{H, F, Cl}$) complexes increases with increasing dipole moment of the LiX molecule [the dipole moments (Kollman *et al* 1970; Latajka and Scheiner 1984) of LiH, LiF and LiCl are 5.88, 6.32 and 7.13 D respectively]. In the $\text{H}_3\text{N} \dots \text{LiH}$ system, inclusion of polarization functions in the basis set does not have any significant effect on its Li-bond energy. The situation is, however, different in the case of $\text{H}_3\text{N} \dots \text{LiF}$ complex where the Li-bond energy is reduced (Latajka and Scheiner 1984) when polarization functions are included. Some *ci* calculations (Latajka and Scheiner 1984) were carried out on this system using the Moller-Plesset perturbation theory to the second order (MP2) and keeping the MO

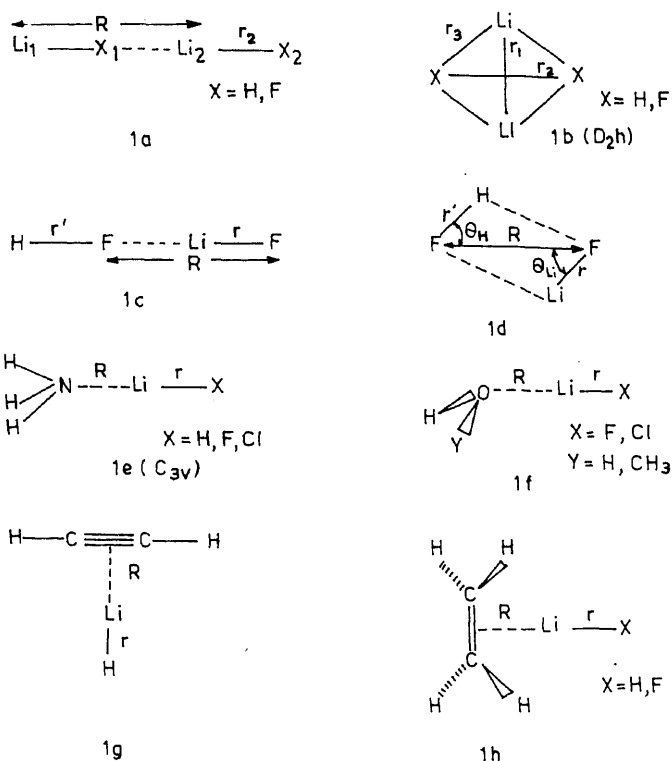


Figure 1. Structure of some Li-bonded dimers.

onding to the inner shells of first-row atoms frozen. The results of this ion indicate that electron correlation does not have any significant effect on the d energy. This is in accord with the observation (Kollman *et al* 1972) made in the case of cyclic $(\text{LiH})_2$.

geometry and Li-bond energy of the $\text{H}_3\text{N} \dots \text{LiF}$ and $\text{H}_3\text{N} \dots \text{LiCl}$ complexes calculated (Kulkarni and Rao 1983) also by using sto-3G basis set. A comparison results with the ones (Latajka and Scheiner 1984) obtained by using larger basis als that the sto-3G calculations underestimate the NLi and LiX bond lengths by 0.1 Å and overestimate the Li-bond energy by about 100%. Errors of able magnitude might have occurred also in the calculations on $\text{H}_2\text{O} \dots \text{LiX}$ (X = F, Cl) and $\text{CH}_3\text{OH} \dots \text{LiX}$ (X = F, Cl) complexes. Thus the sto-3G basis set to be inadequate for a quantitative description of the Li-bonded systems. neless, the results are useful for making a qualitative comparison of the ies of a related series of complexes.

ing our attention back to the sto-3G results of the $A \dots \text{LiX}$ ($A = \text{NH}_3, \text{H}_2\text{O}, \text{H}; X = \text{F, Cl}$) complexes we find that for a given halide the Li-bond energy es in the order $\text{H}_3\text{COH} < \text{H}_3\text{N} < \text{H}_2\text{O}$. The dipole moments of these molecules ry in the same order. It is further observed that for a given electron donor (A) rms stronger Li-bond than LiF (recall that the dipole moment of LiCl is higher at of LiF). The stretching of the LiX bond varies roughly from 0.01 to 0.02 Å in ous $A \dots \text{LiX}$ complexes.

ogous to π -hydrogen bonds (Del Bene 1974) π -lithium bonds are formed by the ion of the LiX dipole with the π -charge cloud of the multiple bonds in les like $\text{C}_2\text{H}_2, \text{C}_2\text{H}_4$ etc. The Li-bond energies in these complexes are relatively $\approx 8\text{--}9$ kcal/mol) and the LiX bond remains virtually unaltered upon complex on.

he basis of the strength of the Li-bonds we can classify the Li-bonded dimers red above roughly into three classes (A, B and C). In class A dimers like $(\text{LiH})_2$ $(\text{LiF})_2$, the Li-bond energy is greater than 25 kcal/mol. These are systems ry strong Li-bonding. In class B dimers like $\text{HF} \dots \text{LiF}$ and $A \dots \text{LiX}$ ($\text{H}_3, \text{H}_2\text{O}, \text{CH}_3\text{OH}; X = \text{H, F, Cl}$) the Li-bond energy lies in the range of 10 to /mol. These are systems with fairly strong Li-bonding. Class C dimers are the π -bonded complexes with Li-bond energy less than 10 kcal/mol. These are with weak Li-bonding. The stretching of the LiX bond increases in the order, $\text{class C} < \text{class B} < \text{class A}$.

size of the basis set is a very important factor in *ab initio* calculations on ded complexes. In general, the DZP basis set seems to be good enough. However, straightforward criterion in this regard is that those basis sets should be used are capable of reproducing the dipole moments of the monomers with ative accuracy. The effect of electron correlation seems to be negligible for composed of highly polar monomer units. But in the π -complexes where one of monomers is a neutral species, dispersion interaction and, hence, electron ion is expected to play a more important role.

Table 2. Population differences in some Li-bonded dimers^{(i), (ii)}.

Dimer	Structure ⁽ⁱⁱⁱ⁾	M_1	X_1	M_2	X_2	Reference
(LiH) ₂	1a	-0.158	+0.032	+0.060	+0.066	Rychlewski and Sabin (1976)
(LiH) ₂	1a	-0.236	+0.366	-0.194	+0.064	Kollman <i>et al</i> (1972)
(LiH) ₂	1b	-0.067	+0.067			Kollman <i>et al</i> (1972)
(LiF) ₂ ^(iv)	1a	-0.083/ -0.128	+0.04/ -0.008	+0.001/ +0.128	+0.042 +0.007	Kollman <i>et al</i> (1970)
(LiF) ₂	1b	+0.007	-0.007			Baskin <i>et al</i> (1973)
(LiF) ₂ ^(iv)	1b	-0.018/ -0.016	+0.018/ +0.016			Kollman <i>et al</i> (1970)
HFLiF ^(iv)	1c	-0.044/ -0.042	+0.034/ +0.012	-0.018/ +0.031	+0.028/ -0.001	Kollman <i>et al</i> (1970)
HFLiF ^(v)	1d	-0.036	+0.041	-0.047	+0.042	Kollman <i>et al</i> (1970)
H ₃ NLiF	1e	-0.070	+0.207	+0.0163	-0.013	Szczesniak <i>et al</i> (1976)
C ₂ H ₄ LiF ^(vi)	1h	-0.047	+0.066	+0.049	+0.007	Szczesniak and Ratajczak (1977)

⁽ⁱ⁾A negative value denotes loss of electron density and a positive value denotes gain of electron density upon dimerisation; ⁽ⁱⁱ⁾ $M = \text{H, Li}$; $X = \text{H, F, N or C}$; ⁽ⁱⁱⁱ⁾for structure see figure 1; ^(iv)without p on Li/with p on Li; ^(v)without p on Li; ^(vi)population difference on the C atom is +0.066.

case of LiH . . . LiH (Kollman *et al* 1972) and HF . . . LiF (Kollman *et al* 1970) yields electron densities which do not obey this criterion. In the cyclic form of (LiH)₂ both the lithium atoms lose electron density, while in (LiF)₂ two opposing trends are predicted by calculations (Kollman *et al* 1970; Baskin *et al* 1973) performed using different basis sets. Since the population analysis is an artifact which is highly sensitive to the choice of basis sets it is not possible to characterise Li-bonds solely on the basis of local charge densities.

A more reliable criterion for the characterisation of Li-bonds is provided by the dipole moment, a quantity which depends not on local (a fictitious quantity) but on global charge distribution. It has been found (Kollman *et al* 1970; Kulkarni and Rao 1983; Latajka *et al* 1984) that the formation of a Li-bond is always accompanied by an increase in dipole moment. Another criterion for the identification of Li-bonds is the change in MO energies of the monomers upon complex formation. It has been observed that those MO of the complex which are mainly centred on the monomer acting as the electron donor are stabilised (more negative orbital energies), and those orbitals which are mainly centred on the monomer acting as the electron acceptor are destabilised. This is a characteristic feature (Kollman and Allen 1969) of donor-acceptor complexes, shared also by Li-bonded dimers.

3. Properties of Li-bonds vis-a-vis those of H-bonds

Umeyama and Morokuma (1977) used an energy decomposition scheme to study the origin of H-bonding. They suggested that at the Hartree-Fock level the stabilisation energy due to H-bonding has three attractive components [Electrostatic (ES), polarisation (PL), charge transfer (CT)], and one repulsive (exchange repulsion, EX) component. They applied this energy partitioning scheme to some Li-bonded dimers as

complex. This implies that in the former system the stabilization energy is derived mainly from the ES interaction while in the latter both ES and CT (to a lesser extent than ES) interactions contribute significantly. In this way they classified the linear form of $(\text{LiH})_2$ as a strong ES > PL, CT complex, the cyclic form of $(\text{LiH})_2$ as a strong ES, CT > PL complex, and the cyclic form of $(\text{LiF})_2$ as a very strong ES $\gg$ PL, CT complex. In general the Li-bonded systems are predominantly ES complexes very much like the strong H-bonded systems like FHF^- , ClHCl^- etc.

Apart from the nature of interactions pointed out above there are a number of similarities and dissimilarities between Li-bonds and H-bonds (Schuster *et al* 1976; Ratajczak and Orville-Thomas 1981). Some of these are as follows.

1. Both H-bonding and Li-bonding involve donor-acceptor type of interaction. This is evident (Kollman and Allen 1969; Kollman *et al* 1970) from the MO energy changes and charge transfer accompanied by the formation of the pertinent complexes.

2. The H-bonds ($Y \dots \text{H}-X$) are linear or nearly so whereas the Li-bonds ($Y \dots \text{Li}-X$) may even be cyclic as in $(\text{LiH})_2$ and $(\text{LiF})_2$. The ease of formation of cyclic structure is due mainly to the low force constant of the LiX bonds.

3. The Li-bonds are quite a bit stronger than the H-bonds due in large part to the higher dipole moment of the LiX subunit.

4. Most hydrogen bonds are known (Schuster *et al* 1976; Ratajczak and Orville-Thomas 1981) to have double minimum potential whereas only single minimum potential is likely to exist for Li-bonds (Szczesniak *et al* 1976). This aspect of Li-bonding has not been properly explored in the *ab initio* calculations reviewed herein.

5. In both H-bonds and Li-bonds, the formation of the complex leads to an elongation of the HX or LiX bonds and consequently a decrease in the stretching frequencies.

6. The $Y \dots X$ distance in the H-bond is invariably shorter (Emsley 1980) than the sum of the van der Waals radii of X and Y . In strong H-bonded systems (Sannigrahi and Peyerimhoff 1984, 1985) like FHF^- this shortening is about 0.5 Å. In the Li-bond the $Y \dots X$ distance is substantially longer than the sum of the van der Waals radii of X and Y . For example, in $\text{H}_3\text{N} \dots \text{LiF}$ and $\text{H}_3\text{N} \dots \text{LiCl}$ complexes (Latajka and Scheiner 1984) the $\text{N} \dots \text{F}$ and $\text{N} \dots \text{Cl}$ distances are 3.66 and 4.12 Å respectively (the corresponding sums of van der Waals radii are 2.95 and 3.30 Å). This difference in the $X-Y$ distance in H-bonded and Li-bonded systems is attributed to the fact that Li^+ (in lithium hydride and halide molecules the net positive charge on Li is close to unity) with a lone pair of electrons cannot penetrate deeply into the charge cloud of the electron donor molecule, while a partially positively charged hydrogen atom can do so because of the smaller size of its charge cloud.

7. The formation of both H-bonds and Li-bonds is accompanied by an increase in dipole moment.

8. The effect of electron correlation is significant in the case of H-bonds (Latajka and Scheiner 1984) and negligible in the case of Li-bonds.

9. The bridging Li-atom gains electron density during complex formation while the bridging H atom loses electron density. As pointed out previously, this is however, not a general characteristic of Li-bonds.

10. Alkyl lithiums can form (Latajka *et al* 1977) Li-bonded complexes with ammonia and aliphatic amines. Similar complexes of alkanes with amines which may involve H-bonding are not known.

4. Concluding remarks

After the above characterisation of H-bonds and Li-bonds the question that naturally arises is: Can sodium also form similar bonds? Obviously, the large size of the charge cloud of Na^+ will be a major hindrance in the formation of a Na-bond. However, if the electrostatic, polarization and charge transfer interactions can overcome the exchange repulsion, then there will be a net stabilisation in energy upon complex formation. *Ab initio* calculations (Baskin *et al* 1973; Kulkarni and Rao 1983) have been reported on a few Na-bonded dimers. Baskin *et al* (1973) have found that $(\text{NaH})_2$, like $(\text{LiH})_2$, can exist in two forms-linear ($C_{\infty v}$) and cyclic (D_{2h}). The cyclic form is more stable than the linear one by about 14 kcal/mol. Moreover the dimerisation energy of $(\text{NaH})_2$ is less than that of $(\text{LiH})_2$ by about 10 kcal/mol (cyclic form) and 3 kcal/mol (linear form). The STO-3G calculations of Kulkarni and Rao (1983) on the $A \dots MX$ ($A = \text{NH}_3, \text{H}_2\text{O}, \text{CH}_3\text{OH}$; $M = \text{H}, \text{Li}, \text{Na}$ and $X = \text{F}, \text{Cl}$) complexes indicate that the strengths of the Na-bonds lie between that of H- and Li-bonds. These calculations (Baskin *et al* 1973; Kulkarni and Rao 1983) also indicate that properties like the changes in MO energies, increase in dipole moment, elongation of the electron acceptor (MX) bond length, charge shift etc., which are associated with Li-bonds, are exhibited by Na-bonds also. Because of higher dipole moments of NaX than LiX molecules the electrostatic interaction in Na-bonded complexes is expected to be stronger than in their Li-bonded counterparts. However, the exchange repulsion in the former outweighs this extra stability gained and as a result Na-bonds are weaker than Li-bonds.

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Currents, kinetic energy, and molecular magnetism

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Abstract. Definitions of current density and kinetic energy density, for a general many-electron system in the presence of an external magnetic field, are carefully discussed and various results are established. In particular, the electronic energy expression has a purely classical interpretation in which every element of the 'charge cloud' behaves like a small magnet, the magnetization depending on the circulation of the induced currents.

Keywords. Quantum mechanics; current density; property densities; magnetic effects.

Introduction

In the discussion of molecular electronic structure and properties, the *electron density* $P(\mathbf{r})$ has always played a central role. For example, as a consequence of the Hellmann-Heynman theorem, $P(\mathbf{r})$ determines the forces exerted on the nuclei by the electron distribution and hence determines the equilibrium geometry of the molecule; it also determines all spin- and velocity-independent first-order properties† and provides a rigorous basis for classical models in which the electron distribution is regarded as a smeared out 'charge cloud' of density $-eP(\mathbf{r})$. Thus, the dipole, quadrupole and higher electric moments, the field gradient at the nuclei, the scattering of x-rays, the electric potential 'seen' by an attacking species at a point outside the molecule can all be calculated *classically* once $P(\mathbf{r})$ is known.

When *spin* is involved (McWeeny 1970), as in the discussion of interactions between the magnetic dipole of the electron and an applied magnetic field, it is useful to introduce a *spin density*. Unlike $P(\mathbf{r})$, which is a scalar density, the spin density is a three-component vector density‡ (Q_x , Q_y , Q_z) such that, for example, $Q_z(\mathbf{r})d\mathbf{r}$ is the contribution to the z-component of total spin angular momentum arising from the volume element $d\mathbf{r}$ at point $\mathbf{r}$. Usually, the z axis is chosen as the direction of an applied magnetic field, and with neglect of spin-orbit coupling effects only one component (Q_z) is non-zero; this describes a uniform 'magnetic polarization' of the charge cloud, along the field direction, in which the density of magnetization at point $\mathbf{r}$ is $-g\mu_B Q_z(\mathbf{r})$ where g is the electronic g -value (2.0023) and μ_B is the Bohr magneton. In the presence of spin-orbit coupling, all components may be non-zero and the magnetization is not generally along the field direction (McWeeny 1973, p. 194).

When velocity-dependent effects are considered (e.g. in discussing interactions between spin dipoles and fields produced by motion of the electron through space) it is

also useful to introduce a (probability) *current density* $\mathbf{J}$ whose components (J_x, J_y, J_z) measure the rate of flow of 'charge' (in electrons per unit volume per unit time), along the three axial directions, at any given point. The corresponding electric current density is simply $-e\mathbf{J}(\mathbf{r})$. In a stationary state described by a real wavefunction, the current density is zero everywhere, but imposition of a magnetic field results in a system of circulating 'induced' currents whose presence is associated with molecular diamagnetism.

For many purposes it follows that a molecule may be regarded as a charge distribution of density $-eP(\mathbf{r})$, with an intrinsic magnetization (in a non-singlet state, $S \neq 0$) of density $-g\mu_B\mathbf{Q}(\mathbf{r})$, containing circulating currents of density $-e\mathbf{J}(\mathbf{r})$. These three fundamental density functions, whose role is discussed more fully elsewhere (McWeeny 1984), may be referred to briefly as 'property densities'. Such densities are not usually observed directly but are defined by reference to an integral whose value yields the actual 'observable', and have consequently been described as 'sub-observables' by Hirschfelder (1978). For example,

$$V_{en} = \int V(\mathbf{r}) P(\mathbf{r}) d\mathbf{r} \quad (1)$$

in which $V(\mathbf{r})$ is the potential energy of an electron of point $\mathbf{r}$ in the field of the nuclei, yields the total electron-nuclear potential energy and this is consistent with the interpretation of $P(\mathbf{r}) d\mathbf{r}$ as the number of electrons in volume element $d\mathbf{r}$.

The aim of this note is to discuss more fully the current density and in particular its connection with the concept of 'kinetic energy density'; and, since non-vanishing currents normally exist only in the presence of an external magnetic field, we shall have to include from the outset the appropriate vector-potential terms in the Hamiltonian. Thus, we shall start from the Hamiltonian

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i,j}' g(i,j) = \sum_i [(\pi^2(i)/2m) + V(i)] + \frac{1}{2} \sum_{i,j}' e^2/(4\pi\epsilon_0) r_{ij} \quad (2)$$

in which

$$\pi(i) = \mathbf{p}(i) + e\mathbf{A}(i) \quad (3)$$

is the 'gauge-invariant' momentum operator for electron i , $\mathbf{A}$ being the magnetic vector potential of the external field, and the other terms have their usual significance.

2. Definitions and difficulties

First we recall that the expectation value of any one-electron quantity, with associated operator $A = \sum_{i=1}^N A(i)$ say, is given by

$$\langle A \rangle = \langle \Psi | \sum_i A(i) | \Psi \rangle = \int [A(1)\rho(\mathbf{x}_1; \mathbf{x}_1')]_{\mathbf{x}_1' = \mathbf{x}_1} d\mathbf{x}_1 \quad (4)$$

where (see, for example, McWeeny and Sutcliffe 1969)

$$\rho(\mathbf{x}_1; \mathbf{x}_1') = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1', \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (5)$$

is the one-electron density matrix, for state Ψ , and $\mathbf{x} (= \mathbf{r}, s)$ is used to denote space and spin variables collectively.

On taking A to be a *spinless* operator, the spin integration in (4) is immediate and we obtain

$$\langle A \rangle = \int [A(1)P(\mathbf{r}_1; \mathbf{r}'_1)]_{\mathbf{r}'_1 = \mathbf{r}_1} d\mathbf{r}_1 \quad (A \text{ spinless}) \quad (6)$$

where

$$P(\mathbf{r}_1; \mathbf{r}'_1) = \int [\rho(\mathbf{x}_1; \mathbf{x}'_1)]_{s'_1 = s_1} ds_1 \quad (7)$$

The electron density in (1) is simply the 'diagonal element' ($\mathbf{r}'_1 = \mathbf{r}_1$) of the spinless density matrix defined in (7): $P(\mathbf{r}) = P(\mathbf{r}; \mathbf{r})$. Evidently it would be possible to describe the integrand in (1), namely

$$V_{en}(\mathbf{r}) = V(\mathbf{r})P(\mathbf{r}), \quad (8)$$

as a 'potential energy density' for the electrons in the field of the nuclei, $V_{en}(\mathbf{r}) d\mathbf{r}$ being the contribution to V_{en} arising from volume element $d\mathbf{r}$ at point $\mathbf{r}$.

We recall that the spin density referred to in §1 plays a similar role in discussing spin properties. Thus, if A represents the z -component of total electron spin, (4) yields

$$\langle S_z \rangle = \int Q_z(\mathbf{r}) d\mathbf{r} \quad (9)$$

in which $Q_z(\mathbf{r})$ is the diagonal element of a *spin* density matrix

$$Q_z(\mathbf{r}_1; \mathbf{r}'_1) = \int [S_z(1)\rho(\mathbf{x}_1; \mathbf{x}'_1)]_{s'_1 = s_1} ds_1 \quad (10)$$

and is evidently the contribution per unit volume, at point $\mathbf{r}$, to the spin angular momentum z component. Components Q_x and Q_y are defined similarly.

If now we take $A(1)$ in (6) to be a component of the velocity operator

$$(1/m)\pi_\alpha = (1/m)(p_\alpha + eA_\alpha) \quad (\alpha = x, y, z) \quad (11)$$

where A_α is the α -component of the magnetic vector potential, we obtain from (6) the total *flux* of electron density in the α -direction in the form

$$\langle \Psi | (1/m) \sum_i \pi_\alpha(i) | \Psi \rangle = \int J_\alpha(\mathbf{r}) d\mathbf{r}. \quad (12)$$

Here $J_\alpha(\mathbf{r})$ is the diagonal element of a *current density matrix*: noting that the expectation value must be real, we have defined

$$J_\alpha(\mathbf{r}) = (1/m) \text{Re} [\pi_\alpha P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (13)$$

as the *local* α -flux at point $\mathbf{r}$. With this definition (see McWeeny and Sutcliffe 1969, p. 226) it is possible to show that the induced* magnetic field due to the current distribution may be calculated using the classical Biot-Savart law. The induced flux density is thus

$$\mathbf{B}_\alpha^{\text{ind}}(\mathbf{r} = 0) = \left(\frac{\mu_0}{4\pi} \right) \int \frac{[\mathbf{r} \times (-e\mathbf{J}(\mathbf{r}))]_\alpha}{r^3} d\mathbf{r} \quad (14)$$

where μ_0 is the magnetic permeability of free space and the point at which the field is required has been used as origin.

It would appear that other property densities could be defined similarly. For

$$T(\mathbf{r}) = (1/2m) [\pi^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (16)$$

which is analogous to (8). In general, however, there are difficulties with such definitions, as has been stressed in particular by Srebrenik and Bader (1975, 1981), in so far as they lack uniqueness; alternative definitions of a property density, leading to the same expectation value when integrated over all space, may give quite different (and even non-real) values *locally*. An example is the current density (13), in which an imaginary component has been discarded merely because its contribution to the *integral* (12) must vanish, π_α being a Hermitian operator. The root of such difficulties is that the reality of expectation values of Hermitian operators (and even the definition of Hermitian character) requires integration over the whole domain of the variables. To obtain acceptable definitions of *local* properties we should start from the Schrödinger equation itself, which does not contain integrations over all space.

3. Point properties. Kinetic energy

Let us start from the time-dependent equation

$$H\Psi = i\hbar(\partial\Psi/\partial t) \quad (17)$$

where, in the presence of the external field, the Hamiltonian (2) may be written

$$H = (1/2m) \sum_i \pi^2(i) + U(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \quad (18)$$

and U contains all the potential energy terms.

We adopt the notation (Nakatsuji 1976)

$$\langle \Psi | (\dots) | \Psi \rangle_n = \int (\dots) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_n, \mathbf{x}_{n+1}, \dots \mathbf{x}_N) \\ \times \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots \mathbf{x}'_n, \mathbf{x}_{n+1}, \dots \mathbf{x}_N) d\mathbf{x}_{n+1} \dots d\mathbf{x}_N, \quad (19)$$

where Ψ^* and Ψ normally contain distinct (primed and unprimed) variables, the last $(N-n)$ of which are identified before performing the integrations. Thus, for example,

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = N \langle \Psi | \Psi \rangle_1 = ND(\mathbf{x}_1; \mathbf{x}'_1),$$

where $D(\mathbf{x}_1; \mathbf{x}'_1)$ is the '1-density' with the Coleman (1963) normalization, namely $\int D(\mathbf{x}_1; \mathbf{x}_1) d\mathbf{x}_1 = 1$.

On multiplying (17) by $\Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots \mathbf{x}'_n)$ and using (19) with $n = 1$, we obtain

$$\langle \Psi | H | \Psi \rangle_1 = i\hbar \int \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots \mathbf{x}_N) \\ \times \frac{\partial \Psi}{\partial t}(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (20a)$$

in which the integrand, with $\mathbf{x}'_1 = \mathbf{x}_1$, would appear to be an energy density since one further integration would yield the expectation value $\langle \Psi | H | \Psi \rangle$. An alternative density, equally acceptable, could be obtained by using the complex conjugate of (17).

Thus,

$$\begin{aligned} \langle H\Psi|\Psi\rangle_1 &= -i\hbar \int \frac{\partial\Psi^*}{\partial t}(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (20b)$$

and the difference of these alternative forms is

$$\langle \Psi|H|\Psi\rangle_1 - \langle H\Psi|\Psi\rangle_1 = i\hbar \frac{\partial D}{\partial t}(\mathbf{x}_1; \mathbf{x}'_1). \quad (21)$$

The two energy densities will thus agree *provided* Ψ is an *exact* stationary state function, for which $i\hbar(\partial\Psi/\partial t) = E\Psi$ and D is time-independent.

Written in full, the first definition (20a) becomes

$$\begin{aligned} \langle \Psi|H|\Psi\rangle_1 &= \int [h(1) + \sum_i g(i, 1) + \sum_j g(1, j)] \\ &\quad \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &\quad + \int \left[\sum_{i=2}^N h(i) + \frac{1}{2} \sum_{i,j=2}^N g(i, j) \right] \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (22)$$

where the second term contains only an $(N-1)$ -electron Hamiltonian. The second definition (20b) leads to a similar result, but with h replaced by $h^\dagger$ throughout, adjoint operators (containing $-i$ in place of i) being understood to work on the *primed* variables of Ψ^* . At this stage, $\mathbf{x}_1$ and $\mathbf{x}'_1$ may be regarded as parameters; Ψ and Ψ^* are still antisymmetric functions of all *other* variables and in the domain of these other variables the Hamiltonian in the second integral of (22) is a Hermitian operator. Consequently, in taking the difference in (21) the second integrals are identical and cancel; and the only terms which remain are

$$\begin{aligned} (1/2m) \int [\pi^2(1) - \pi'^2(1')] \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\ \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N = i\hbar \frac{\partial D(\mathbf{x}_1; \mathbf{x}'_1)}{\partial t}. \end{aligned}$$

Since the integrations on the left also yield $D(\mathbf{x}_1; \mathbf{x}'_1)$ this result gives, with the more usual normalization,

$$(1/2m) [\pi^2 \rho(\mathbf{x}; \mathbf{x}') - \pi'^2 \rho(\mathbf{x}; \mathbf{x}')]_{\mathbf{x}'=\mathbf{x}} = i\hbar \frac{\partial \rho(\mathbf{x})}{\partial t} \quad (23)$$

In the absence of spin operators, a further spin integration gives

$$(1/2m) [\pi^2 p(\mathbf{r}; \mathbf{r}') - \pi'^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} = i\hbar \frac{\partial P(\mathbf{r})}{\partial t}. \quad (24)$$

It now appears, remembering (16), that the difference between the two energy densities in (21) arises from a difference of two *kinetic-energy* densities; for an exact stationary

state the time derivative in (24) vanishes and the two definitions

$$T(\mathbf{r}) = (1/2m)[\pi^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (25a)$$

$$T'(\mathbf{r}) = (1/2m)[\pi'^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (25b)$$

yield identical densities at all points in space.

Let us now expand the density matrices in (25) in terms of any complete set of one-electron functions $\{\chi_r\}$. Thus

$$P(\mathbf{r}; \mathbf{r}') = \sum_{r,s} P_{rs} \chi_r(\mathbf{r}) \chi_s^*(\mathbf{r}') \quad (P_{sr} = P_{rs}^*) \quad (26)$$

and the two kinetic-energy densities become

$$T(\mathbf{r}) = (1/2m) \sum_{r,s} P_{rs} \chi_s^*(\mathbf{r}) \pi^2 \chi_r(\mathbf{r}) \quad (27a)$$

$$T'(\mathbf{r}) = (1/2m) \sum_{r,s} P_{rs} [\pi^2 \chi_s(\mathbf{r})]^* \chi_r(\mathbf{r}) \quad (27b)$$

The difference between these two expressions may now be written in terms of the current density by using appropriate identities.

First we note that a 'generalized current', of which (13) is the real part, may be defined as

$$\mathbf{J}(\mathbf{r}) = (1/2m)[\pi P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} = \mathbf{J}_R(\mathbf{r}) + i\mathbf{J}_I(\mathbf{r}) \quad (28)$$

where, on using (26), it follows that

$$\mathbf{J}_R(\mathbf{r}) = (\hbar/2mi) \sum_{r,s} P_{rs} [(\nabla \chi_r) \chi_s^* - \chi_r (\nabla \chi_s)^*] + (e/m) \mathbf{A} \sum_{r,s} P_{rs} \chi_r \chi_s^* \quad (29a)$$

$$\mathbf{J}_I(\mathbf{r}) = -(\hbar/2m) \sum_{r,s} P_{rs} [(\nabla \chi_r) \chi_s^* + \chi_r (\nabla \chi_s)^*] = -(\hbar/2m) \nabla P(\mathbf{r}). \quad (29b)$$

Then, in (27), we write

$$\chi_s^* \pi^2 \chi_r = (\hbar/i)^2 \chi_s^* \nabla^2 \chi_r + (e\hbar/i) [2\mathbf{A} \cdot (\chi_s^* \nabla \chi_r) + \chi_s^* \chi_r (\nabla \cdot \mathbf{A})] + e^2 A^2 \chi_s^* \chi_r \quad (30a)$$

$$\chi_r (\pi^2 \chi_s)^* = (\hbar/i)^2 \chi_r \nabla^2 \chi_s^* - (e\hbar/i) [2\mathbf{A} \cdot (\chi_r \nabla \chi_s^*) + \chi_r \chi_s^* (\nabla \cdot \mathbf{A})] + e^2 A^2 \chi_r \chi_s^* \quad (30b)$$

and make use of the identities

$$\nabla \cdot (\chi_r \nabla \chi_s^*) = (\nabla \chi_r) \cdot (\nabla \chi_s^*) + \chi_r \nabla^2 \chi_s^*,$$

and

$$\nabla \cdot (\chi_s^* \nabla \chi_r) = (\nabla \chi_s^*) \cdot (\nabla \chi_r) + \chi_s^* \nabla^2 \chi_r,$$

which give on subtraction

$$\nabla \cdot [\chi_r \nabla \chi_s^* - \chi_s^* \nabla \chi_r] = \chi_r \nabla^2 \chi_s^* - \chi_s^* \nabla^2 \chi_r. \quad (31)$$

On putting (30a, b) into (27a, b) and using (31) we obtain, after rearranging and introducing $\mathbf{J}_R$ defined in (29a),

$$T(\mathbf{r}) - T'(\mathbf{r}) = (\hbar/i) \nabla \cdot \mathbf{J}_R(\mathbf{r}). \quad (32)$$

on (24) is thus equivalent to a conservation condition for the current density:

$$\operatorname{div} \mathbf{J}_R(\mathbf{r}) = -\frac{\partial P(\mathbf{r})}{\partial t}. \quad (33)$$

of probability density out of any region, computed using the *real* current $\mathbf{J}_R$, is the rate of decrease of the probability of finding an electron in that region. The above results apply to any exact solution of the many-electron Schrödinger equation (17). For a stationary state, in particular, P is time-independent, the divergence of $\mathbf{J}_R$ is everywhere zero, and the two kinetic-energy densities become real and identical. Evidently, the physical interpretation of $\mathbf{J}_R$ (with components defined as in (27a, b)) is entirely justified; and the agreement of (27a, b) shows that the kinetic energy density defined in (14) has at least a degree of uniqueness, *provided* the wavefunction represents an exact stationary state.

Even generally, with non-exact or time-dependent wavefunctions, there remains the question of how to define a unique and real kinetic-energy density. The most obvious proposal would be to adopt the *mean* of the two forms in (27a, b), which is evidently the real part of a complex density; and it then readily follows (using identities such as (30))

$$\bar{T} = (T + T')/2 = T_0 + (\hbar/2) \operatorname{div} \mathbf{J}_I + e\mathbf{A} \cdot \mathbf{J}_R - (e^2/2m) A^2 P \quad (34)$$

where the imaginary component of the generalized current density is given in (29b),

$$T_0(\mathbf{r}) = (1/2m) [\mathbf{p} \cdot \mathbf{p}^\dagger P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (35)$$

where the dagger as usual indicates that the second operator works on the primed wavefunction. The density $T_0(\mathbf{r})$, integrated over any domain Ω , gives the kinetic energy contribution introduced by Srebnik and Bader (1975, 1981) for assigning an energy density to a finite 'subspace'. Thus, with the convention that the $\mathbf{x}_i$ integration extends over the domain Ω ,

$$\langle T_0 \rangle_\Omega = (1/2m) \int_\Omega \sum_i \mathbf{p}^\dagger(i) \Psi^* \cdot \mathbf{p}(i) \Psi \, d\mathbf{x}_1 \dots d\mathbf{x}_N. \quad (36)$$

As proposed by Srebnik and Bader, however, even in the field-free case which they considered, integration of the density $\bar{T}$ provisionally defined in (34) does not yield the result (36); for the $\operatorname{div} \mathbf{J}_I$ term in (34) also gives a contribution which is generally non-zero. Thus (using σ to denote the surface of Ω and dS for a surface element)

$$(\hbar/2) \int_\Omega \operatorname{div} \mathbf{J}_I d\mathbf{r} = -(\hbar^2/4m) \int_\Omega \nabla^2 P d\mathbf{r} = -(\hbar^2/4m) \int_\sigma (\nabla P) \cdot d\mathbf{S}. \quad (37)$$

This quantity vanishes when Ω is the whole of space, since P and its derivatives go to zero at infinity; and it also vanishes for the 'zero-flux surfaces' used extensively by Bader and his co-workers. But it is not at all clear whether (34) or (35) provides the more 'correct' kinetic energy density from an interpretive point of view, even when $\mathbf{A} = \mathbf{0}$, and there are further complications when the field-dependent terms are admitted.

Equation (35) suggests the way to proceed. In the presence of the field, we make the substitution $\mathbf{P} \rightarrow \boldsymbol{\pi}$ and consider the eligibility of the quantity

$$T_A(\mathbf{r}) = (1/2m) [\boldsymbol{\pi} \cdot \boldsymbol{\pi}^\dagger P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (38)$$

so that (35) corresponds to the field-free case $\mathbf{A} = \mathbf{0}$. To obtain a more illuminating form we may start from (26) and use the identity

$$\begin{aligned} (\pi\chi_r) \cdot (\pi\chi_s) &= \hbar^2 (\nabla\chi_r) \cdot (\nabla\chi_s^*) + i\hbar(e\mathbf{A}\chi_r) \cdot (\nabla\chi_s^*) - i\hbar(\nabla\chi_r) \cdot (e\mathbf{A}\chi_s) + e^2 A^2 \chi_r \chi_s^* \\ &= \hbar^2 (\nabla\chi_r) \cdot (\nabla\chi_s^*) + (e\hbar/i) \mathbf{A} \cdot [\chi_s^* \nabla\chi_r - \chi_r \nabla\chi_s^* + (ie/\hbar) \mathbf{A} \chi_r \chi_s^*]. \end{aligned}$$

On multiplying both sides by $(1/2m)P_{rs}$ and summing over r and s , the result will clearly be $T_A(\mathbf{r})$. The square-bracket term in the identity would lead to $\mathbf{J}_R$ of (29a) if the imaginary part were doubled; we therefore add and subtract an extra term $(ie/\hbar)\mathbf{A}\chi_r\chi_s^*$ and, on proceeding as indicated find

$$T_A(\mathbf{r}) = T_0(\mathbf{r}) + e\mathbf{A} \cdot \mathbf{J}_R(\mathbf{r}) - (e^2/2m)A^2 P(\mathbf{r}). \quad (39)$$

The dependence on the field and on the induced current density is exactly as in (34), but the term $(\hbar/2) \operatorname{div} \mathbf{J}_I$ which leads to the surface term (37) is absent.

To summarize: $T_A(\mathbf{r})$ is real everywhere, yields the usual kinetic energy when integrated over all space [in agreement with that given by (16)], and shows a correct dependence on current density, electron density and vector potential at all points. Expression (38) appears to offer the most useful definition of a kinetic-energy density for a system in the presence of a magnetic field, described by a wavefunction which is not necessarily exact.

4. Physical interpretations. Discussion

It remains only to discuss the interpretation and status of (39) and the significance of its disagreement with the mean-value definition (34), both forms being consistent with the principles of quantum mechanics as usually stated. The difference between the two expressions is

$$T_f(\mathbf{r}) = T(\mathbf{r}) - T_A(\mathbf{r}) = (\hbar/2) \operatorname{div} \mathbf{J}_I(\mathbf{r}) = -(\hbar^2/4m) \nabla^2 P(\mathbf{r}), \quad (40)$$

which may be regarded as a 'fictitious' kinetic-energy density. This quantity has no observational significance and its presence results only from the use of a *variational* expression for the kinetic energy (i.e. from integrations over all space or a finite domain): in this sense its origin is purely mathematical and has nothing to do with electronic *motion*. The justification for this view is, in essence, contained in the work of Bader and collaborators (Srebrenik and Bader 1980). The kinetic energy of the whole system is obtained by integrating $\bar{T}$ in (34) over the infinite domain, in which case the term (37) vanishes and both $\bar{T}$ and T_A lead to the correct result. The contribution from T_f does not in fact arise *within* the domain, finite or infinite, but only at the *surface*. It is only when the Schrödinger equation (17) is viewed as the Euler equation for a variational principle that the question of the surface terms arises; when the Lagrangian density is written in a form which contains the usual kinetic energy operator, the stationary value condition *even for a finite region* leads to the Schrödinger equation *provided the surface terms are included*. Whereas for an infinite region the surface terms automatically vanish (and may thus be disregarded) their presence generally ensures that the variational principle, applied to a *finite* region, would yield the same results as direct solution of the Schrödinger equation. The feasibility of using regional variational

by choosing *particular* regions bounded by zero-flux surfaces. From the point of physical interpretations, however, there seems to be no case for treating the T_A terms as part of the kinetic energy itself; and we therefore adopt T_A , as given in (39), as the kinetic-energy density.

A -dependent terms in (39) have an interesting physical significance; they yield, on integrating over all space, the exact energy contribution arising from imposition of the magnetic field (up to terms quadratic in field components). To show this, we assume the wavefunction in the absence of the field is Ψ_0 (for $A = 0$) and that in switching the field $H_0 \rightarrow H = H_0 + \lambda H'$ and

$$\Psi_0 \rightarrow \Psi = \Psi_0 + \lambda \Psi' + \dots (\lambda \rightarrow 1) \quad (41)$$

Ψ' is exact to first order in field. It is well known that the function Ψ , which is *not* normalized, does not give the true second-order energy as an expectation value of the Hamiltonian; the correct second-order part of the energy is $\langle \Psi_0 | H' | \Psi' \rangle$, or equivalently $\langle \Psi' | H' | \Psi_0 \rangle$, whereas $\langle \Psi | H | \Psi \rangle$ with Ψ given in (41) gives a second-order term $\langle \Psi_0 | H' | \Psi' \rangle + \langle \Psi' | H' | \Psi_0 \rangle$ which is too large by a factor of 2. The correct result could, however, be obtained by using, instead of (41), the function

$$\tilde{\Psi} = \Psi_0 + \frac{1}{2} \lambda \Psi', \quad (42)$$

which yields (noting that $\langle \Psi_0 | H_0 | \Psi' \rangle = 0$)

$$\begin{aligned} E &= \langle \tilde{\Psi} | (H_0 + \lambda H') | \tilde{\Psi} \rangle \\ &= \langle \Psi_0 | H_0 | \Psi_0 \rangle + \lambda \langle \Psi_0 | H' | \Psi_0 \rangle + \frac{1}{2} \lambda^2 [\langle \Psi_0 | H' | \Psi' \rangle \\ &\quad + \langle \Psi' | H' | \Psi_0 \rangle], \end{aligned} \quad (43a)$$

or, in other words

$$E = E_0 + \lambda E' + \lambda^2 E''. \quad (43b)$$

Result (43b) may be justified by renormalizing (41) to *second* order, using the normalized function to compute the energy, and eliminating the $\langle \Psi' | \Psi' \rangle$ term by reference to the perturbation equations.

Advantage of introducing (42) is that the energy may then be written in terms of terms associated with the function $\tilde{\Psi}$: and in particular,

$$\tilde{P} = P_0 + \frac{1}{2} \lambda P' \quad (44)$$

which (taking the true *first-order* density change) will yield the correct expectation value, to first order, of the one-electron terms in the Hamiltonian.

We now express (43b) in terms of the 'renormalized' density. The leading term is $E_0 = T_0 + V_0$, where V_0 is the potential energy of the unperturbed system while T_0 is referring to the unperturbed system and therefore depending only on P_0 , is simply the first term in the expression (39) for the kinetic energy in the presence of the field. The total electronic energy may thus be written $E = V_0 + T_A$ where T_A contains A -dependent terms (linear and quadratic) which appear in (43a). The result is valid for $\lambda = 1$ from now on and remembering that field components serve to separate the terms

$$E = E_0 + e \int \mathbf{A} \cdot \mathbf{J}(\mathbf{r}) d\mathbf{r} - (e^2/2m) \int A^2 P(\mathbf{r}) d\mathbf{r}. \quad (45)$$

In this expression the components of $\mathbf{J}$ are derived from (44) using (13); but in the last term we may put $P = P_0$ since $\mathbf{A}$ is already of first order in field components and inclusion of the second term in (44) would therefore lead to third-order effects. On separating $\mathbf{J}$ into its two parts we thus obtain

$$E = E_0 + e \int \mathbf{A} \cdot \mathbf{J}_0(\mathbf{r}) d\mathbf{r} + e \int \mathbf{A} \cdot \mathbf{J}_1(\mathbf{r}) d\mathbf{r} - (e^2/2m) \int A^2 P_0(\mathbf{r}) d\mathbf{r} \quad (46)$$

where

$$\mathbf{J}_0(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p} P_0(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}}, \quad (47a)$$

$$\mathbf{J}_1(\mathbf{r}) = (1/m) \operatorname{Re} [e \mathbf{A} P_0(\mathbf{r}; \mathbf{r}') + \mathbf{p} P'(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}}. \quad (47b)$$

Clearly, $\mathbf{J}_0(\mathbf{r})$ is the current density in the zero-field limit and leads to a 'permanent' magnetic moment i.e. to true paramagnetism; it is non-zero only for atoms and other systems of high symmetry in which there may be unquenched angular momentum. $\mathbf{J}_1(\mathbf{r})$, on the other hand, is linear in field components (P' being of first order) and is therefore connected with *induced* currents; but it is *not* the field proportional part of the true current density, which would be obtained using $P = P_0 + \lambda P' + \lambda^2 P'' + \dots$, instead of (44), in the expression (13).

To obtain a more transparent form of (46) it is sufficient to combine the last two terms. The result may be written

$$E = E_0 - \int \mathbf{A} \cdot (-e \mathbf{J}_0(\mathbf{r})) d\mathbf{r} - (1/2) \int \mathbf{A} \cdot (-e \mathbf{J}_{\text{ind}}(\mathbf{r})) d\mathbf{r} \quad (48)$$

in which $\mathbf{J}_0(\mathbf{r})$ is defined in (47) while $\mathbf{J}_{\text{ind}}(\mathbf{r})$ is the field-proportional part of the current density derived from the exact density matrix $P = P_0 + P' + P'' + \dots$, according to (13); thus

$$\mathbf{J}_0(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p} P_0(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}}, \quad (49a)$$

$$\mathbf{J}_{\text{ind}}(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p} P'(\mathbf{r}; \mathbf{r}') + e \mathbf{A} P_0(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}}, \quad (49b)$$

and describes the system of induced currents produced by application of the field. The two field-dependent terms in (48) represent, respectively, the potential energy of a system of 'permanent' currents of density $-e \mathbf{J}_0(\mathbf{r})$, and that of a system of induced currents of density $-e \mathbf{J}_{\text{ind}}(\mathbf{r})$, in a magnetic field of vector potential $\mathbf{A}$. Both terms are entirely classical in form, even though the currents themselves are calculated from quantum mechanics. It is also worth remarking that there is no 'gauge problem': the complete current

$$\mathbf{J}(\mathbf{r}) = \mathbf{J}_0(\mathbf{r}) + \mathbf{J}_{\text{ind}}(\mathbf{r}) \quad (50)$$

contains the gauge invariant operator $\boldsymbol{\pi}$ and is invariant against change of origin of the vector potential; and this property is shared by the separate terms in (49) and by the energy contributions to which they lead in (48). This is not the case in the traditional approach (see for example Davies 1967) where magnetic properties are almost invariably calculated as a difference of 'diamagnetic' and 'paramagnetic' contributions which individually have no invariant physical interpretation.

When the applied field is uniform, the first- and second-order terms take a very familiar form. On putting $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$, the $\mathbf{J}_0$ -term in (48) immediately becomes

$$E' = -\mathbf{B} \cdot \boldsymbol{\mu}_{\pi}^0 \quad (51)$$

where μ_m^0 is the (permanent) magnetic dipole moment, with components

$$\mu_{m\lambda}^0 = -\mu_B \int \text{Re}[L_\lambda P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} \quad (52)$$

in which L_λ is a (dimensionless) angular momentum component. The corresponding form of the second-order energy term is

$$E'' = -\frac{1}{2} \mathbf{B} \cdot \mu_m^{\text{ind}} = \frac{1}{2} \mathbf{B} \cdot \alpha^m \cdot \mathbf{B} \quad (53)$$

where

$$\mu_{m\lambda}^{\text{ind}} = \sum_{\mu} \alpha_{\lambda\mu}^m B_{\mu} \quad (54)$$

represents an *induced* magnetic moment whose components are related to the field components through the magnetic polarizability tensor α^m . Expressions for the tensor components are easily found on writing P in the more explicit form

$$P = P_0 + P' = P_0 + B_x P_x + B_y P_y + B_z P_z \quad (55)$$

where P_x , for example, is the density change per unit applied field in the x direction, and can be calculated by any appropriate form of perturbation theory. On putting (55) in (48) and using the result to evaluate the final term in (48) we at once find (53), with

$$\alpha_{\lambda\mu}^m = -\mu_B \int \text{Re}[L_\lambda P_{\mu}(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r}. \quad (56)$$

In comparison with (52) it is clear that $\alpha_{\lambda\mu}^m$ is the λ -component of the magnetic dipole associated with the density change P_{μ} due to unit field in the μ direction. The interpretation of the factor $1/2$ in (53) is also classical: with $\mu^{\text{ind}} = \mu^{\text{ind}}(\mathbf{B})$, the energy gain in a field increase $d\mathbf{B}$ is $d\mathbf{B} \cdot \mu^{\text{ind}}(\mathbf{B})$ and on allowing the field to increase from 0 to its final value integration at once gives (53).

In conclusion, it is worth remarking that realistic *ab initio* calculations of current density, at least at the Hartree-Fock level, are now computationally feasible and provide valuable insight into the magnetic properties of molecules (Lazzeretti and Zangwill 1981).

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space symmetry adaptation of crystal orbitals

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Abstract. Symmetry adaptation of crystal orbitals normally means that one constructs functions transforming according to the irreducible representations of a space group. In the present paper we discuss certain drawbacks with such a procedure and point out the need for a method which avoids the detour into reciprocal space.

Keywords. Symmetry adaptation; crystal orbital; direct space; generalized Wannier function; localization.

Introduction

Connection between the concepts of localization, orthonormalization and symmetry adaptation of crystal orbitals has been analyzed in two recent papers (Calais 1985, 1986). The three properties associated with these concepts are all desirable for use in calculations of the electronic structure of solids. Symmetry adaptation of a set of functions is a well defined procedure described in most text books on group theory. It can be carried out in different ways, though, and this is an aspect which will be discussed in the present paper. Symmetry adapted orbitals associated with different symmetries are by definition orthogonal. If they belong to the same symmetry one must however invoke some type of orthogonalization procedure. Both symmetry adaptation and orthogonalization involve mixing of functions, and inasfar as functions are localized atomic orbitals both procedures may therefore lead to an increase in delocalization. The relation between localization and orthogonalization is rather subtle and it seems a little premature to claim that the two are mutually exclusive (Levy and Berthier 1977).

Symmetry adaptation traditionally used for crystal orbitals is based on the irreducible representations of the group of the wave vector (Cornwell 1969; Bradley and Cracknell 1972). This group is used both for symmorphic groups, where it is a subgroup of the point group associated with the space group, and for non-symmorphic groups, where it is the translation group as a subgroup, and thus forms a subgroup of the space group. Bradley and Cracknell (1972) distinguish these two groups by the terms 'little co-group of the wave vector' (a subgroup of the point group) and 'little group of the wave vector' (a subgroup of the space group).

In a symmorphic group the irreducible representations are of the form

$$D(\{R|\mathbf{m}\}) = e^{i\mathbf{k} \cdot \mathbf{m}} \Gamma(R), \quad (1)$$

where $\Gamma(R)$ is an irreducible representation of the little co-group of $\mathbf{k}$. We use the standard notation for space group elements with R denoting the point group

operation and $\mathbf{m}$ a translation (which is always primitive for a symmorphic group). Its operation on a vector $\mathbf{r}$ is given by

$$\{R|\mathbf{m}\}\mathbf{r} = R\mathbf{r} + \mathbf{m}. \quad (2)$$

For non-symmorphic groups the construction of the irreducible representations is a little more complicated, but there also we need the irreducible representations of the group of the wave vector—with the meaning ‘little group of $\mathbf{k}$ ’. Of all these irreducible representations only those satisfying

$$\Gamma^{(p)}(\{1|\mathbf{m}\}) = e^{-i\mathbf{k} \cdot \mathbf{m}} \Gamma^{(p)}(\{1|0\}), \quad (3)$$

are however useful in the sense that the basis functions associated to them can be used to form basis functions for the space group.

This traditional approach has dominated the scene since these concepts and procedures were introduced in the thirties. It is the natural approach if one works in reciprocal space and is primarily interested in the extended eigenfunctions of the one electron Hamiltonian. A ‘complementary’ perspective based on direct space concepts has always existed, and this approach has been gaining ground in recent years (Anon 1980), both as an alternative way of handling the ordinary band theory problem (Calais 1985b; von Boehm and Calais 1979), and as the more natural way of treating problems where the translation symmetry is no longer present.

This direct space perspective requires a different way of handling the symmetry adaptation. Very important work has been done in that area by, among others, des Cloizeaux (1963, 1964) and Zak (1980; 1981a,b). Probably because relatively few scientists seem to have been interested in this type of problem much remains to be done, however. In the present paper we review some of the drawbacks of the ‘traditional approach’ (§2) and some aspects of the results obtained so far ‘in direct space’ (§3). In the last section we discuss several possibilities of reaching the final goal. In particular we try to point out what ingredients of the presently known procedures are likely to be valuable.

The paper is thus of an exploratory nature which should not be surprising since the problems encountered are not yet solved in a way leading to simple efficient procedures for creating a set of *completely orthonormal, symmetry adapted crystal orbitals*. We hope that the discussions in this paper will stimulate further work towards that goal.

2. Problems in the traditional formulation

A basis of atomic like orbitals localized in ordinary space is definitely preferable for a number of problems in solid state physics (Anon 1980). It is desirable to take maximum advantage of the symmetry of the crystal, and the overlap problem must be handled in one way or another. At the same time one must try to avoid that symmetry adaptation and orthogonalization destroy the localization of the original functions completely. It is still an open question whether these requirements are compatible or not.

One possible procedure is described earlier (Calais 1985a). Starting out from a set of atomic orbitals (AO) $\phi_{\lambda}(\mathbf{m}, \mathbf{r})$, localized (or rather labelled) by the unit cell index $\mathbf{m}$ and the compound subscript λ standing for position in the unit cell and type of orbital, one first finds the irreducible components $\phi_{\lambda}^{\mathbf{k}}(\mathbf{r})$ with respect to the little co-group $\bar{G}^{\mathbf{k}}$ of a wave vector $\mathbf{k}$. This means that the functions $\phi_{\lambda}^{\mathbf{k}}(\bar{\mathbf{r}})$ transform according to the s th row

of the irreducible representation (IR) Γ_p of $\bar{G}^{\mathbf{k}}$. Then one forms Bloch sums of these functions, which are thus symmetry adapted both to $\bar{G}^{\mathbf{k}}$ and to the translation group. The resulting Bloch sums are orthogonal with respect to the three symmetry labels $\mathbf{k}$, p , s but *not* with respect to λ . In order to get a basis for an IR of the full space group one must also operate on the Bloch sums with the representatives of the star of $\mathbf{k}$. For each set of symmetry labels we now have a set of functions labelled by λ with a non unit overlap matrix. In Calais (1985a) it is proposed to make a symmetric orthonormalization of these functions in order to get a set of completely orthonormal, symmetry adapted functions.

The functions constructed according to this prescription are Bloch functions, which implies that they are extended throughout the crystal. Given a set of Bloch functions $\psi(\mathbf{k}, \mathbf{r})$ with $\mathbf{k}$ running through the whole first Brillouin zone (BZ) one can construct an associated set of Wannier functions by means of the unitary transformation,

$$W(\mathbf{m}_j, \mathbf{r}) = [1/(N)^{1/2}] \sum_{\mathbf{k}}^{\text{BZ}} \psi(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{m}}. \quad (4)$$

As proposed by von Boehm and Calais (1984) this can be done also with the completely orthonormal, symmetry adapted functions described earlier. The resulting functions will at least be *labelled* by the unit cell index $\mathbf{m}$. Whether they still possess any local properties is an open question.

The procedure just described means that we start out in ordinary space, make a detour in reciprocal space, and then return to ordinary space. The reason for this 'detour' is the fact that the IR of a space group are characterized by—among other symbols—the wave vectors $\mathbf{k}$ in BZ. Another way to describe this detour is to say that out of localized functions (in ordinary space) we first form extended ones which are finally combined to functions which are again somehow localized.

The most cumbersome 'technical' problem in this procedure is probably the final orthonormalization. First one has to calculate—for a fairly large number of wave vectors and for all symmetry species of the corresponding little co-groups—the overlap matrices. Each such matrix has to be diagonalized so that one can construct the inverse half power of it, which is necessary for the symmetric orthonormalization. There are other methods for constructing $\Delta^{-1/2}$ but in general we can hardly expect a power series expansion to be sufficient. Thus the proposed procedure suffers primarily from a drawback 'on principle'. There are also certain technical problems, which, although perfectly tractable, make the method less attractive. At least intuitively it would seem possible to achieve the same or an equivalent goal in a more direct way.

3. Direct space concepts

In a paper of far reaching importance des Cloizeaux (1963) has shown that symmetry adapted *local* orbitals can be used for analysis of the eigenfunctions of a one electron crystal Hamiltonian. A central concept in his method is the group G_M containing all those elements of the space group G which leave the point M invariant. G_M is thus a subgroup of the full space group. The Wannier functions which are associated with M form a basis for an IR of G_M . Since G_M is a subgroup of G , one can subduce representations of G_M (in general reducible) from the IR of G .

Building on the results obtained by des Cloizeaux, Zak (1980, 1981a,b) has

developed a number of very interesting concepts which deserve to be used much more widely than has been the case so far. In particular he has stressed the need for a representation which describes the symmetry of a band *as a whole*. A band in connection is always an *isolated* band. In general it contains several branches which touch at some points or along some lines in $\mathbf{k}$ space. In a given band there is a fixed number of states associated with each wave vector $\mathbf{k}$. All the Bloch functions associated with such an f -fold band span its *band space*. It is then possible to construct functions in this space which transform according to what Zak calls a *band representation* of the space group.

The band representation is a somewhat elusive concept which needs to be analysed further. It is related to the representations of the 'local' groups G_M of des Cloizeaux. Being a subgroup of the full space group G one can make a coset decomposition with respect to G_M . If the band representations of G_M are known one can induce them to G . The band representation is closely connected with the symmetry of the Wannier functions. Direct and reciprocal space are inseparable precisely for symmetry reasons. Concepts associated with the wave vector are central to the construction of the IR of the space group. Still the concepts just sketched—the local group G_M , which forms the counterpart in direct space to the group of the wave vector, and the band representations—would seem to provide raw material for a more 'direct' symmetry adaptation in ordinary space.

4. Discussion

des Cloizeaux (1963) has outlined a procedure for constructing what he calls generalized Wannier functions. He chooses a point M_0 and introduces a set of orbitals centred at M_0 which form a basis for an IR of G_{M_0} . The space group elements generate the points M which form the lattice of M_0 . From the orbitals centred at M_0 he constructs the corresponding orbitals centred at M . He also shows that all these orbitals (a set at each lattice point) are completely orthonormal. Their localization is a rather more difficult problem which des Cloizeaux has treated in subsequent papers (des Cloizeaux 1964).

The starting point for this procedure is a set of orthonormal functions which form a basis for an IR of G and for those IR of G_{M_0} which are subduced from it. The 'traditional' method (Calais 1985a) provides bases for the IR of G , and out of those one can construct the required starting functions. This is in fact the method developed in (von Boehm and Calais 1984). As indicated earlier it has certain drawbacks.

The combination of symmetric and successive orthonormalization proposed by Löwdin (1956) avoids these drawbacks, since it works exclusively in ordinary space. The price to pay gets rather high, though. Given a lattice with a set of p orbitals in each unit cell, one first constructs symmetrically orthonormalized orbitals for each type of orbital. Efficient methods for doing that exist (Löwdin *et al* 1960; Calais and Auer 1964). The result is a set of p functions 'in' each unit cell such that functions of the same type in different unit cells are orthogonal, whereas functions of different type belonging to the same and in different unit cells are not. Expressed in another way we have p sets of orbitals such that within each set the orbitals are orthonormal. Löwdin (1956) proposed to make a successive orthonormalization of the *sets* in cases when that is motivated 'physically'. One can certainly apply any type of orthonormalization to the *sets* in a

achieve the goal: completely orthonormal orbitals. If the number p is small this procedure is certainly feasible and it has been used in practice. It does however involve a very large number of functions of all the overlap matrices and it gets quite cumbersome when p increases. It can certainly be combined with symmetry adaptation and then the successive orthonormalization will require special treatment.

Thus it is easy to 'create local symmetry' or to form functions which like the Wannier functions are orthonormal if centred in different unit cells. What is difficult is to combine both procedures.

A possible path might involve a combination of des Cloizeaux and Löwdin's methods. The former can prove a number of important results because he starts out with rather far reaching assumptions. The latter's procedures can be applied directly to a given material, but since they easily get rather cumbersome it would be very useful if they could be simplified by means of some group theoretical results.

The term 'type of orbital' which has been used here refers both to position in the unit cell and to the particular function centred there. Any position in a unit cell can serve as a starting point for a lattice and a combination of local symmetry adaptation and des Cloizeaux' methods would seem promising. On the other hand we must also be able to handle the case when a set of positions in a unit cell are suitable centres for orbitals and it is not immediately clear how to apply his procedures in such a case.

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Semiempirical calculation of static molecular polarizability using some benzene derivatives and aromatic heterocycles

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Abstract. The static polarizability of fifteen organic molecules (point group symmetry: C_{2v} ; number of electrons ≥ 26) have been theoretically calculated using the CNDO/S-CHFT scheme and the results have been compared with other available data.

Keywords. Static polarisability; CNDO/S; CHFT.

Introduction

Calculation of electric polarizability, both static and dynamic, of large molecular systems have drawn considerable attention in recent times (Marchese and Jaffe 1977; Ali-Khamiri and Hamerka 1979; Waite and Papadopoulos 1983; Gupta and Bhattacharyya 1984a). In this context, the CNDO/S-CI method (Delbene and Jaffe 1968) combined with second order perturbation theory (Marchese and Jaffe 1974) has been found to be quite promising insofar as inclusion of electron correlation and vibrational effects are concerned. In view of the facts that (i) the CNDO/S-CI method (Delbene and Jaffe 1968) is actually equivalent to working in the Tamm-Dancoff approximation (TDA) (Dunning and McKoy 1967) of the equations of motion (EOM) (Gardi *et al* 1977) approach and (ii) the TDA involves only the correlated excited states and not the ground state, it is natural, therefore, to seek a theory which incorporates the effect of electron correlation in both the ground and excited states. The Hartree-Fock-theory (CHFT) is one that provides a satisfactory route to this

problem. Here, we report a few exploratory calculations of static molecular polarizability using the CNDO/S-CHFT scheme, i.e., where the basis functions are generated by the CNDO/S approximation and the static polarizability is computed using the CHFT.

Theory

Theoretical aspects have been discussed in detail elsewhere (Gupta and Bhattacharyya 1984b). However, for convenience, the essential points are outlined

$$(H_0 + V)|\psi\rangle = E|\psi\rangle, \quad (1)$$

we extract the Rayleigh-Schrodinger perturbation equations as

$$(H_0 - E_0)|0\rangle = 0, \quad (2)$$

$$(H_0 - E_0)|\psi^{(1)}\rangle + (V - E^{(1)})|0\rangle = 0, \quad (3)$$

etc., where the terms have their usual significance. The second-order correction to energy is given by

$$E^{(2)} = \langle 0|V|\psi^{(1)}\rangle. \quad (4)$$

By defining the excitation (de-excitation) operator $S^\dagger(S)$ as

$$S^\dagger|0\rangle = |\psi^{(1)}\rangle \quad (5a)$$

and

$$S|0\rangle = 0, \quad (5b)$$

we can proceed through (3) to obtain

$$[H_0, S^\dagger]|0\rangle + (V - E^{(1)})|0\rangle = 0. \quad (6)$$

$E^{(2)}$ may then be written in a commutator form as

$$E^{(2)} = \langle 0|[V, S^\dagger]|0\rangle, \quad (7)$$

and the polarizability (α) is given by

$$\alpha = 2 E^{(2)}. \quad (8)$$

Now (6) may be rearranged to yield

$$[S, [H_0, S^\dagger]]|0\rangle + [S, V]|0\rangle = 0 \quad (9)$$

and the use of the triple commutator $[S, H_0, S^\dagger]$, (McCurdy *et al* 1977) yields

$$\langle 0|[S, H_0, S^\dagger]|0\rangle + \frac{1}{2}\langle 0|[V, S^\dagger]|0\rangle + \frac{1}{2}\langle 0|[S, V]|0\rangle = 0 \quad (10)$$

from (9).

At this point the ground state wavefunction $|0\rangle$ is approximated as $|\phi_{HF}\rangle$, $S^\dagger$ is considered a linear combination of $(1h-1p)$ excitation and de-excitation operators:

$$S^\dagger = \sum_{\alpha m} \langle m|g|\alpha\rangle a_m^\dagger a_\alpha - \sum_{n\beta} \langle \beta|h|n\rangle a_\beta^\dagger a_n,$$

and V is taken as

$$V = \sum_{ij} \langle i|v|j\rangle a_i^\dagger a_j$$

where m, n , etc denote particle orbitals, $\alpha, \beta, \dots$ the hole orbitals and $i, j, \dots$ any orbital. These are precisely the approximations used in deriving the RPA (McCurdy *et al* 1977) and we can proceed in the same way to arrive at (11):

$$\sum_{n\beta} A_{m\alpha, n\beta} \langle n|g|\beta\rangle + B_{m\alpha, n\beta} \langle \beta|h|n\rangle + \frac{1}{2} \langle m|V|\alpha\rangle = 0. \quad (11)$$

matrix elements are given by

$$A_{m\alpha, n\beta} = (\varepsilon_m - \varepsilon_n) \delta_{mn} \delta_{\alpha\beta} + \{1 + (-1)^s\} \langle m\beta | v | \alpha n \rangle - \langle m\beta | v | n\alpha \rangle, \quad (12a)$$

$$B_{m\alpha, n\beta} = \{1 + (-1)^s\} \langle mn | v | \alpha\beta \rangle - \langle mn | v | \beta\alpha \rangle, \quad (12b)$$

where s represents the spin state.

Equation (11), along with (6), is identical with the CHFT equation deduced by Hoffmann *et al* (1966). We have used here these very equations to evaluate different principal components of α .

Results and discussion

In Table 1 we report the results of ground-state calculations of the polarizability components ($\alpha_{\mu\mu}$) and the mean polarizability ($\bar{\alpha}$) for 15 molecules, all having at least 8 atoms, 26 electrons and C_{2v} point group symmetry. Our results are also compared with CNDO/S-CI values (Marchese and Jaffe 1977) and experimental data wherever available. In all these calculations $\{\alpha\}$ and $\{m\}$ have 10 orbitals each.

It is interesting to note that usually $\alpha_{\mu\mu}$ ($\mu = x, y$ or z) values calculated by the CNDO/S-CHFT scheme are lower than those obtained via the CNDO/S-CI scheme. However, we should mention that whereas the CNDO/S-CI describes correlated excited

Table 1. Ground-state polarizability components (α_{xx} , α_{yy} , α_{zz}) and average polarizability ($\bar{\alpha}$) of some planar molecules with C_{2v} symmetry (in units of 10^{-24} cm³), calculated by the CNDO/S-CHFT method.

Molecule	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
Benzene	9.377 (13.19) ^a [11.1] ^b	9.387 (13.50) [11.1]	1.008 (0.90) [7.4]	6.591 (9.20) [9.87]
Pyridine	9.200 (12.16)	8.807 (12.82)	0.97 (1.02)	6.326 (8.67)
Pyridazine	8.775 (13.32)	9.147 (12.73)	1.188 (1.76)	6.370 (9.27)
Pyrimidine	7.944 (11.86)	8.431 (12.16)	1.155 (1.58)	5.843 (8.53)
Pyrazine	8.138 (12.06)	7.460 (13.34)	1.239 (1.14)	5.612 (8.85)
s-Triazine	8.269	8.239	1.197	5.902
s-Tetrazine	8.344	9.588	1.568	6.500
Pyrrrole	4.870	8.250	1.290	4.803
Furan	6.824	6.977	1.489	5.097
Fluoro-benzene	9.871	9.587	0.965	6.808
1,4-Difluorobenzene	10.077	9.461	0.866	6.801
1,3-Difluorobenzene	10.505	9.997	0.835	7.112
1,2-Difluorobenzene	9.965	10.599	0.642	7.069
p-Benzoquinone	3.107	19.404	0.844	7.785
Aniline	9.195	9.865	1.344	6.801

^a CNDO/S-CI values³ in parenthesis; ^b experimental values in square brackets; A D Buckingham and N L Bridges 1966, Proc. R. Soc. (London) A295, 324.

states only by a maximum of 60 configurations (Marchese and Jaffe 1977), our CNDO/S-CHFT prescription introduces electron correlation into *both* the ground and excited states through 100 configurations. Besides, various semi-empirical calculations for planar molecules using all-valence AO basis sets indicate (Teixeira-Dias and Sarre 1975) that (i) the calculated out-of-plane polarizability component (α_{zz}) is always *much less* than the experimental value, and (ii) the $\{\alpha_{\mu\mu}\}$ are always *smaller* than the corresponding experimental values; however, the values improve gradually with the extension of the AO-basis set (Gupta and Bhattacharyya 1984a).

Table 1 shows that in the case of *benzene*, the molecule for which experimental data is available, the $\alpha_{\mu\mu}$ (CNDO/S-CHFT) $< \alpha_{\mu\mu}$ (experimental) $< \alpha_{\mu\mu}$ (CNDO/S-CI), $\mu = x$ or y , which corroborates the remark mentioned above. This, in turn, implies that CNDO/S-CHFT is probably more balanced than the CNDO/S-CI.

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Geometry optimization of acetonitrile monomer and dimers using CNDO/force method

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Abstract. The geometry optimization of monomeric acetonitrile and its dimers is carried out using CNDO/force method. The results are compared with the experimental and already reported theoretical parameters.

Keywords. Geometry optimization; CNDO/force; acetonitrile monomer and dimers.

1. Introduction

As of now, the structure of acetonitrile is still ambiguous. Dielectric polarization studies (Buckingham and Raab 1961) predict a dipole moment of 2.67 D for the gaseous dimer at 80° and suggest an anti-parallel alignment of the two molecules. Viscosity data (Saum 1966) suggest that in liquid acetonitrile, association does not exceed dimer level. The appreciable polar interaction is also evident from the large negative heat and entropy of dimerisation derived from second virial coefficient measurements (Lambert *et al* 1949; Prausnitz and Carter 1960). Molecular association in liquid acetonitrile is evidenced by spectroscopic studies. Matrix isolated infrared spectra on acetonitrile (Freedman and Nixon 1972) propose various structures for the acetonitrile dimer and favour an anti-parallel alignment of the CN groups based on IR assignments. Raman spectral studies (Givan and Loewenschuss 1983) of matrix isolated acetonitrile suggest the formation of a dimer involving interaction between the methylic hydrogens and the nitrile nitrogen, in addition to the centro-symmetric dimer. Molecular orbital studies have been reported for various associated species. Linear, anti-parallel and displaced anti-parallel structures were studied by CNDO/2 calculations (Paoloni and Hauzer 1975; Paoloni and Dagnino 1975; Gramstad and Tjessem 1977). *Ab initio* studies have been reported for head-to-tail and anti-parallel dimer structures (Dagnino *et al* 1976). In a series of papers from our group (Kanakavel *et al* 1976; Annamalai and Surjit Singh 1982a, b, c 1983a, b; Annamalai *et al* 1978, 1984; Jothi *et al* 1982; Brakaspathy *et al* 1985; Brakaspathy and Surjit Singh 1985), we have employed the CNDO/force method to evaluate geometrical parameters and force fields of various complex polyatomic molecules. We thought it of interest to use this method for geometry optimization of the dimeric species of acetonitrile.

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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2. Computational details

CNDO/force calculations are performed using a modified form (Kanakavel *et al* 1976) of the computer program CNINDO of Pople and Beveridge (1970). The optimization is carried out using the 'steepest descent method' proposed by Pulay and Torok (1973). In this method, the forces acting on each atom are computed for the experimental geometry of the molecule by analytically differentiating the total energy calculated using CNDO wave functions with respect to nuclear coordinates. The forces are then allowed to relax towards equilibrium by a small distance say 0.01 Å. The forces are computed again for the new geometry. This process is repeated till the norm of the forces reaches the preset value. During iterations, both the energy and the norm of the forces keep decreasing and when the norm of the forces is less than 0.001, it is found that further iterations do not alter the geometry of the molecule. This geometry is taken as the optimized geometry. All the calculations are done on an IBM 370/155 computer.

3. Results and discussion

The optimized geometry of the acetonitrile monomer is given in table 1. The geometrical parameters obtained in this method agree well with the experimental (Matsumura *et al* 1962) and *ab initio* values (Lien *et al* 1983; Edgecombe and Boyd 1983). The total energy of -27.89975 a.u. for acetonitrile monomer calculated using the CNDO/force method is better than the reported CNDO/2 value of -26.0869 a.u. (Gramstad and Tjessem 1977). There is a slight increase in C-C and C≡N bond lengths when compared to experimental values. However, the total energy calculated using this method is found to be higher than the STO-3G *ab initio* value (-130.27154 a.u.). Such discrepancies in energies calculated by *ab initio* and semiempirical methods have been already reported in literature (Pople and Beveridge 1970).

Four different structures are considered for the acetonitrile dimer viz, displaced anti-parallel, anti-parallel, hydrogen bonded and head-to-tail (figure 1). The geometry optimization is carried out in two stages. In the first stage, the intermolecular distance is optimized whereas in the second stage iterations are carried out on the whole species. For the displaced anti-parallel dimer, the displacement of the two molecules (*l*) was also optimized before optimizing the complete geometry. The variations of energy with

Table 1. Optimized geometry^a of acetonitrile monomer.

Description	CNDO/ force	Experimental ^b	STO-3G ^c	3-21G ^d
R_{C-C}	1.4213	1.4583	1.486	1.457
$R_{C\equiv N}$	1.1920	1.1571	1.154	1.139
R_{C-H}	1.1187	1.1036	1.088	1.083
$\angle HCC$	110.85	109.45	109.9	110.1
Total energy	-27.89975	—	-130.27154	-131.19060

^a bond lengths in Å, bond angles in degrees and energies in atomic units; ^b Matsumura *et al* 1962; ^c Lien *et al* 1983; ^d Edgecombe and Boyd 1983

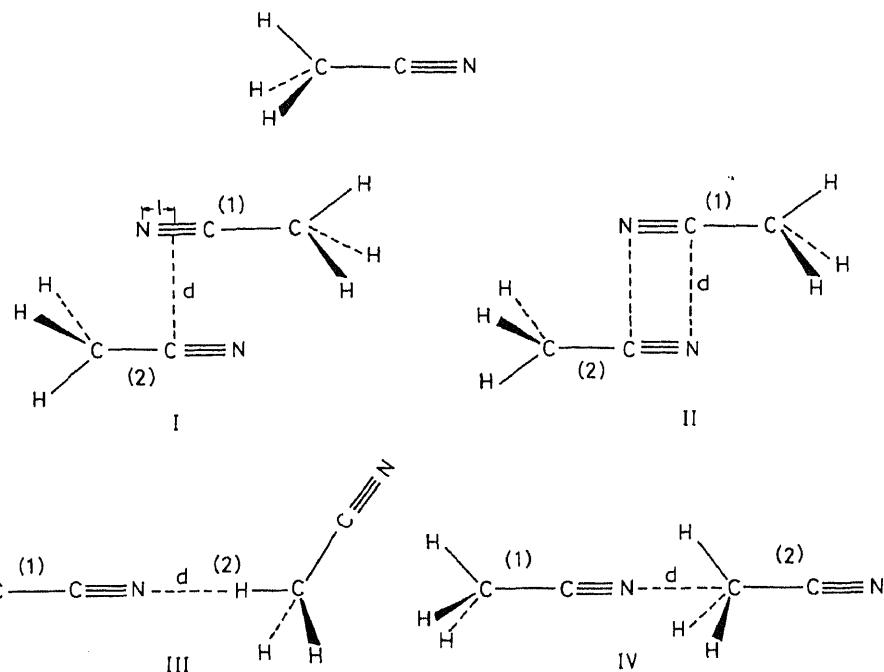


Figure 1. Structure of acetonitrile monomer and various dimers; displaced anti-parallel dimer (I), anti-parallel dimer (II), hydrogen bonded dimer (III) and head-to-tail dimer (IV).

molecular distance (d) and displacement (l) for the dimers considered are given in table 2. The optimized geometries of the four dimers are given in table 2. It is noticed from table 2 that the displaced anti-parallel dimer has the lowest energy (−55.33672 a.u.). The intermolecular and the displaced distances are 2.2034 Å and 0.8 Å respectively. The energy of the displaced dimer is better than the reported value of −55.7926 a.u. (Gramstad and Tjessem 1977). The reported intermolecular and displaced distances are 2.0 Å and 0.8 Å respectively. The interaction with the π -bond of the nitrile group increases the $C\equiv N$ bond length. This may be explained by the increase in the CN bond length from 1.1920 Å for the monomer to 1.1953 Å for the dimer. The C–C and C–H bond lengths also get affected as shown in table 2. The anti-parallel dimer has the next best energy with the value of −55.0864 a.u. Since the interaction is through C–N dipoles, both the nitrile groups of the dimer are affected to the same extent. This is evident from the symmetrical increase in the nitrile bond lengths from 1.1920 Å to 1.1953 Å. The intermolecular distance for this dimer is calculated to be 2.1991 Å. The C–C and C–H bond lengths are also affected similarly. The hydrogen-bonded dimer has an energy of −55.80512 a.u.; the bonded C–H bond length changes from 1.1920 to 1.1921 Å while the nitrile group of the other molecule decreases to 1.1911 Å. The bonded C–H bond length increases from

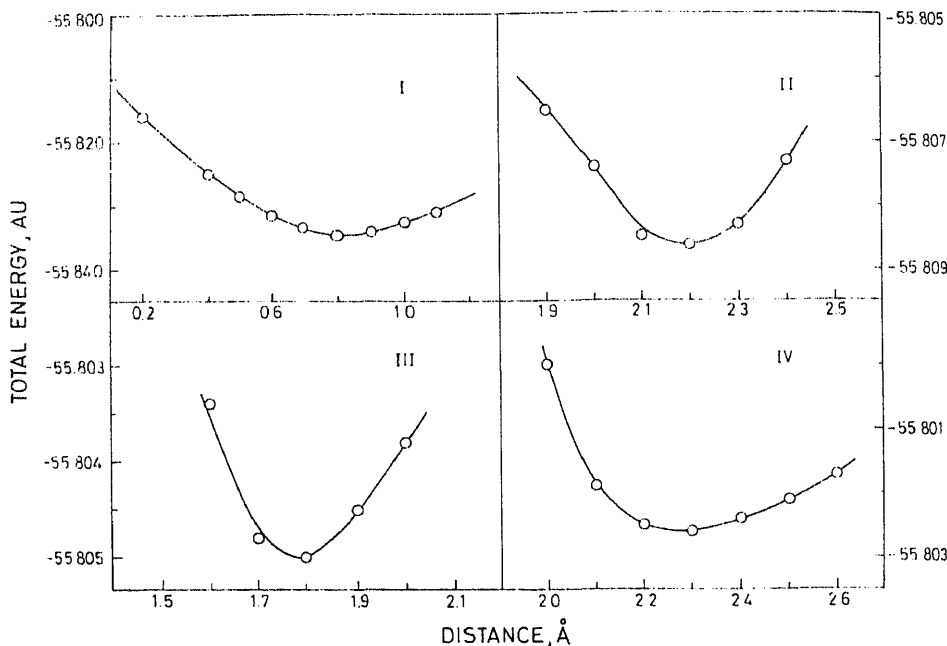


Figure 2. Variation of energy with displacement (*l*) for displaced anti-parallel structure (I) with $d = 2.2$ Å and with intermolecular distance (*d*) for anti-parallel (II), hydrogen-bonded (III) and head-to-tail (IV) structures respectively.

Table 2. Optimized geometries^a of acetonitrile dimer.

Description	Displaced anti-parallel	Anti-parallel	Hydrogen bonded	Head-to-tail
RC-C (1)	1.4301	1.4228	1.4211	1.4217
RC-C (2)	1.4301	1.4228	1.4209	1.4257
RC≡N (1)	1.2041	1.1953	1.1921	1.1930
RC≡N (2)	1.2090	1.1953	1.1911	1.1914
RC-H ₁ (1)	1.1204	1.1206	1.1181	1.1187
RC-H ₂ (1)	1.1204	1.1190	1.1186	1.1187
RC-H ₃ (1)	1.1204	1.1190	1.1186	1.1187
RC-H ₁ (2)	1.1204	1.1205	1.1292	1.1193
RC-H ₂ (2)	1.1204	1.1190	1.1186	1.1192
RC-H ₃ (2)	1.1204	1.1190	1.1186	1.1192
RN...x (<i>d</i>)	2.2034	2.1991	1.7914	2.2940
RC...π (1)	0.8021			
Total energy	-55.83672	-55.80864	-55.80512	-55.80293
Bonding energy	-5.19062	-5.16253	-5.15902	-5.15682
-Δ <i>H</i> _S	23.35	5.74	3.53	2.15

^astabilization energies in kcal mol⁻¹ other units as in table 1. Bond angles were also calculated but are not included here for the sake of brevity. The data can be obtained from the authors on request.

^b (1) and (2) in parentheses denote molecules 1 and 2, respectively as shown in figure 1.

8 Å. It is generally observed that the intermolecular distance calculated by *ab initio* is higher than that calculated by semiempirical methods in associated species (Murthy *et al* 1970). The bonded CN bond length increases to 1.1930 Å while the other nitrile bond increases slightly to 1.1914 Å. The C-C and C-H bond lengths experience slight increases. In all these models, it is noticed that interaction through the CN bond invariably weakens the bond. These results justify the decrease in $\nu_{\text{C}\equiv\text{N}}$ from the gas to the liquid states (2267.0 to 2252.5 cm^{-1}) (Thomas and Orville-Thomas 1969).

The stabilization energy ($-\Delta H_s$) at the energy minimum for all the four models is calculated using the CNDO/force method. The displaced anti-parallel model has the highest stabilization energy of 23.35 kcal.mole $^{-1}$. This stabilization energy is better than the value calculated from the reported energies of monomer and dimer acetonitrile using CNDO/2 method (13.55 kcal mol $^{-1}$) (Gramstad and Tjessem 1977). The anti-parallel dimer has the next higher stabilization energy (5.74 kcal mol $^{-1}$) which is higher than the CNDO/2 value (4.49 kcal mol $^{-1}$) (Paoloni and Dagnino 1975) as well as the *ab initio* value (1.6802 kcal mol $^{-1}$). (Dagnino *et al* 1976). The stabilization energy of the hydrogen bonded dimer is calculated to be 3.53 kcal mol $^{-1}$. The head-to-tail dimer has the least stabilization energy (2.15 kcal mol $^{-1}$). The reported CNDO/2 and *ab initio* values for the head-to-tail dimer are 2.39 kcal mol $^{-1}$. (Paoloni and Dagnino 1975) and 0.94 kcal mol $^{-1}$ (Dagnino *et al* 1976) respectively.

It may be noticed from the above discussion that the stabilization energies of the dimers as well as the binding energies of various species calculated by the CNDO/force method are not comparable to the *ab initio* values. However, comparative studies of these energies can well be utilised to predict the most stable conformers. Further, the CNDO/force values are found to be better than the CNDO/2 values reported earlier. The geometrical parameters obtained are comparable with the previous results.

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Mixed valency in the high-temperature phases of transition metal molybdates, $AMoO_4$ ($A = Fe, Co, Ni$)†

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Abstract. Transition metal molybdates of the formula $AMoO_4$ where $A = Fe, Co$ or Ni exhibit a first-order phase transition between 670 K–970 K. An investigation of the low-temperature (LT) and high-temperature (HT) phases by x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, magnetic susceptibility and other physical methods shows that the phase transition is associated with a valence change of the type $A^{2+} + Mo^{6+} \rightleftharpoons A^{3+} + Mo^{5+}$ in the cases of iron and cobalt molybdates.

Keywords. Transition metal molybdates; mixed valency; high-temperature phases.

Introduction

Trivalent transition metal molybdates $AMoO_4$, where $A = Fe, Co$ or Ni , crystallize under ambient conditions in a defect rocksalt structure (LT phase) with the transition metal ions in octahedral coordination (Smith and Ibers 1965). These molybdates undergo first-order phase transitions at high temperatures (670–970 K) with a large change (6%) in volume (Sleight and Chamberland 1968). The high temperature (HT) phase can be quenched in the case of the iron compound. The structure of the HT phase has not been determined but powder diffraction data reveal that the HT phase is isostructural with $MnMoO_4$ (Abrahams and Reddy 1965; Sleight *et al* 1968) wherein Mn is in octahedral and Mo in tetrahedral coordination. The main structural change associated with the phase transition appears to be a change in Mo coordination from six to four. Since the transition occurs only in $FeMoO_4$, $CoMoO_4$ and $NiMoO_4$ and not in the other divalent metal molybdates (Sleight and Chamberland 1968), it has been suspected that the transition may involve valence change of the type, $A^{2+} + Mo^{6+} \rightleftharpoons A^{3+} + Mo^{5+}$. We have prepared $AMoO_4$ molybdates of Fe, Co and Ni and characterized both the HT and LT phases by x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, Mössbauer spectroscopy, magnetic susceptibility and electrical resistivity measurements besides x-ray crystallography. The results reveal that the transition is likely to be associated with a valence change of the cations at least in the cases of iron and cobalt molybdates and that the HT phases are mixed valent as described, by $_{1-x}A^{3+}Mo^{6+}_xMo^{5+}_xO_4$.

2. Experimental

FeMoO_4 was prepared by heating the required quantities of Fe, Fe_2O_3 and MoO_3 in a sealed tube at 1270 K for 48 hours. Depending on the cooling rate, either the HT or the LT phase was obtained (Sleight *et al* 1968). The pure LT phase was obtained by slow cooling, first to room temperature and then to liquid nitrogen temperature. The HT phase was obtained by quenching the sealed tube from 870 K to room temperature.

LT phases of CoMoO_4 and NiMoO_4 were prepared by heating stoichiometric quantities of nickel oxide or cobalt oxalate respectively with MoO_3 at 1270 K for 48 hours in air, followed by slow cooling to room temperature (Sieber *et al* 1983). HT phases of CoMoO_4 and NiMoO_4 could not be obtained by quenching from high temperatures. HT CoMoO_4 could, however, be prepared (Chojnacki *et al* 1974) by precipitating $\text{CoMoO}_4 \cdot x\text{H}_2\text{O}$ through the addition of cobalt(II) nitrate to a solution of ammonium paramolybdate at a pH of 5.5 and heating the precipitate at 670 K for 18 hours in air. HT NiMoO_4 could not be prepared by this precipitation method.

Formation of compounds and their phase purity were ascertained by x-ray powder diffraction (Philips PW 1050/70 diffractometer). The unit cell parameters agree with the reported values of the HT and LT phases of the AMoO_4 compounds (Sleight *et al* 1968).

The HT-LT transition of AMoO_4 was studied by differential scanning calorimetry (Perkin-Elmer, Model 2) using indium as standard. X-ray photoelectron spectra (xps) were reported using an ESCA-III mark 2 spectrometer with Al $K\alpha$ radiation. X-ray absorption spectra were recorded using a bent crystal spectrograph; analysis of the spectra was carried out by using a Carl-Zeiss MD-100 microdensitometer. Magnetic susceptibility measurements were made in the 15-1000 K range using a Faraday balance. Electrical resistivity of pressed pellets of FeMoO_4 was measured using the four-probe technique. Room temperature (300 K) Mössbauer spectra were recorded using 25 mc/ ^{57}Co (Rh) source; the spectra were least-squares fitted assuming Lorentian line shape.

3. Results and discussion

All the three molybdates undergo a first-order phase transition showing an exothermic peak in DSC or DTA. The transition temperatures are in the order, Fe (650 K) < Co (780 K) < Ni(990 K). It is interesting that the transition temperature correlates with the stability of the trivalent oxidation states of the A metal atoms; Ni(III) is the least stable and the transition temperature of NiMoO_4 is the highest. This is also consistent with the inability to quench the HT phase of NiMoO_4 . The transitions were irreversible in DSC/DTA in all the three cases. The heats of transition estimated from the area under the peak are 5.8, 3.6 and 2.5 kJ mol $^{-1}$ for the iron, cobalt and nickel compounds respectively.

X-ray photoelectron spectra (xps) of the LT phases of all the three molybdates show the presence of Mo^{6+} and A^{2+} cations as illustrated in figure 1 with a Mo($3d_{5/2}$) binding energy of 232.6 eV characteristic of Mo^{6+} (Sarma and Rao 1980; Rao *et al* 1978). xps of the HT phases of FeMoO_4 and CoMoO_4 show evidence for the presence of mixed valent Mo and Fe/Co as illustrated in figure 1. Thus, in the Mo($3d$) region there is a shoulder on the lower binding energy side of the Mo($3d_{5/2}$) peak at 231.8 eV due to

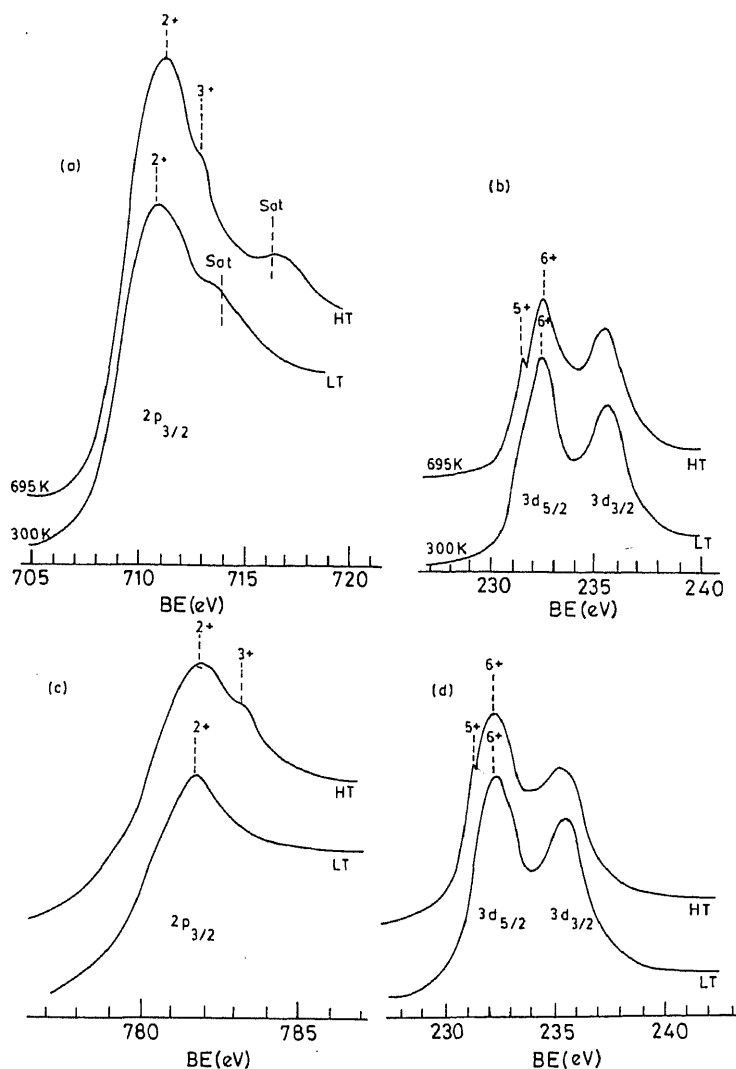


Figure 1. XPS of $A\text{FeMoO}_4$ molybdates. (a) $\text{Fe}(2p)$ spectra of LT and HT FeMoO_4 ; (b) $\text{Mo}(3d)$ spectra of LT and HT FeMoO_4 . The corresponding Co and Mo spectra of CoMoO_4 are shown in (c) and (d).

peaks in the case of HT FeMoO_4 is 60:40. The spectra in the $\text{Fe}(2p)$ and $\text{Co}(2p)$ ions also show changes indicating the coexistence of 2+ and 3+ ions.

For FeMoO_4 and LT CoMoO_4 show characteristic satellites at 3.5–4.0 eV and 6.2 eV respectively in the Fe/Co ($2p$) spectra similar to FeO and CoO (Rao *et al* 1978). In HT FeMoO_4 the satellite is at 5.5 eV confirming the presence of Fe^{3+} (Vasudevan *et al* 1978). A similar change is observed in the $\text{Co}(2p)$ spectrum of HT CoMoO_4 .

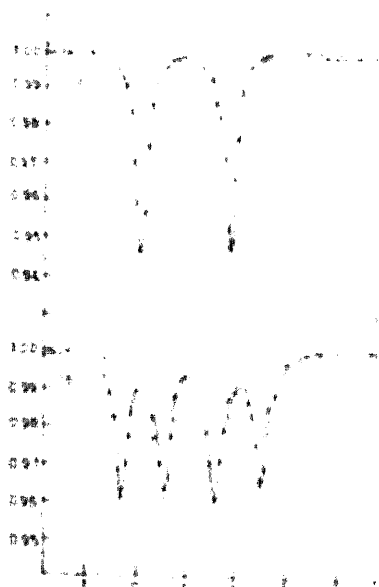
states of transition metals (Satoke *et al.* 1979). The shifts in the case of the d -metal states are listed in table 1. The chemical shifts in the K edges of both the M and d metal ions in 1:1 phases are consistent with M^{2+} and d^{1+} states (Satoke *et al.* 1979; Martin *et al.* 1980). The Mo K -edge shows a smaller chemical shift in the 1:1 phases; correspondingly, the Fe and Co edges show larger chemical shifts in comparison to the phases consistent with the presence of d^{1+} ions as well.

The Mossbauer spectrum of 1:1 $FeMoO_4$ at room temperature displays a two-finger pattern similar to that reported with an isomer shift of 0.02 mm/sec and a quadrupole splitting of 1.77 mm/sec² (Sleight *et al.* 1968). The spectrum is consistent with the presence of high spin Fe^{2+} in 1:1 $FeMoO_4$. The Mossbauer spectrum of 1:1 $FeMoO_4$ shows a four-finger pattern indicating the presence of two sets of iron atoms (figure 2b). The spectrum of 1:1 $FeMoO_4$ has been attributed to two different kinds of iron sites both containing high spin Fe^{2+} (Sleight *et al.* 1968). Considering high spin and

Table 1. Chemical shifts of the K absorption edges of the d - MoO_4 metal phases

Compound	Chemical shift in eV (eV ²)	
	d ion	Mo ion
1:1 $FeMoO_4$	6.4	13.9
1:1 $FeMoO_4$	10.4	13.1
1:1 $CoMoO_4$	7.8	13.3
1:1 $CoMoO_4$	9.4	12.9
1:1 $NiMoO_4$	6.9	13.9

Source: Martin *et al.* (1980).



belonging to one type of iron and lines 2 and 4 as belonging to another set of iron atoms, we derive isomer shifts of 1.45 and 0.57 mm sec⁻¹ with quadrupole splittings of 0.97 and 1.91 mm sec⁻¹ respectively. These results can be taken to support the existence of Fe²⁺ and Fe³⁺ ions in the HT phase in agreement with xps and absorption edge measurements. The large quadrupole splittings may be due to a highly distorted environment around the iron atoms.

Magnetic susceptibility of the molybdates was measured in the 15-1000 K range to characterize the phase transition. FeMoO₄ was sealed in an evacuated silica tube to prevent oxidation. Susceptibilities of the other two molybdates were determined in vacuum (10⁻⁴ torr). The χ_m^{-1} - T (K) plots (figure 3) give μ_{eff} (and θ values in parentheses) of 4.98 (28), 4.76 (10) and 3.40 (24) for the LT phases of Fe, Co and Ni molybdates, respectively, consistent with their formulation as $A^{2+}\text{Mo}^{6+}\text{O}_4$ with divalent Fe and Co in the high-spin states. FeMoO₄ and CoMoO₄ show a sharp decrease in the susceptibility beyond the transition and the μ_{eff} values of the HT phases (~1.4 BM) are smaller than those expected for either A^{3+} (HS) Mo^{5+}O_4 or $A_{1-x}^{2+}\text{Mo}_x^{3+}$ (HS) $\text{Mo}_{1-x}^{6+}\text{Mo}_x^{5+}\text{O}_4$. One possibility is that the Fe³⁺ and Co³⁺ are in the low-spin state. However, it is more likely that this is due to the itinerant nature of *d*-electrons

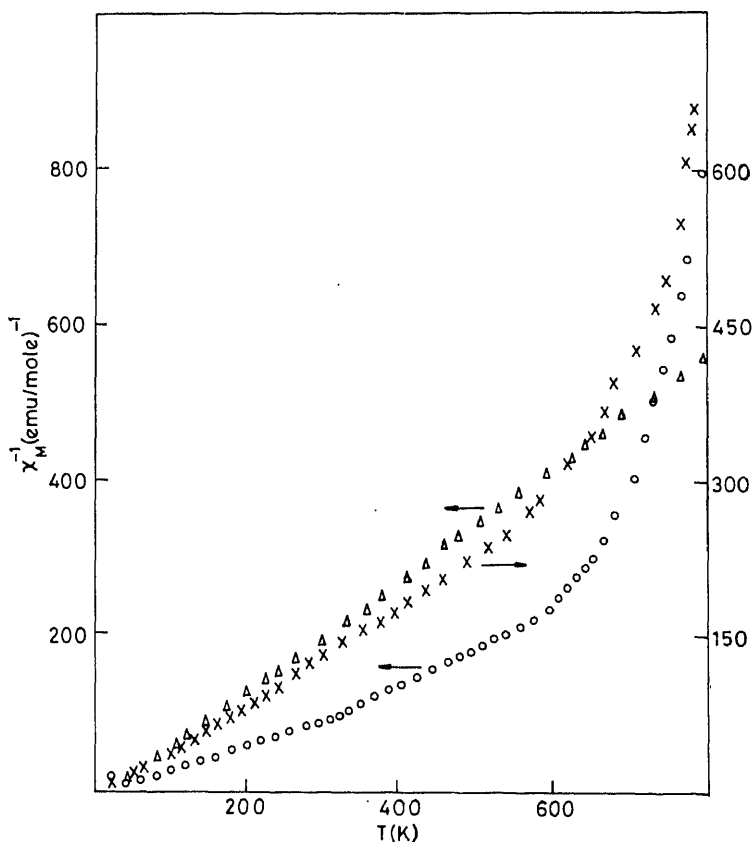


Figure 3. χ_m^{-1} - T (K) plots of FeMoO₄ (circles), CoMoO₄ (crosses) and NiMoO₄ (triangles).

in the m phases. Accordingly, we do find that m-FeMoO₄ shows a considerably lower electrical resistivity ($\approx 80 \text{ ohm-cm}$) than r-FeMoO₄ ($\approx 3 \times 10^3 \text{ ohm-cm}$), the lower resistivity of m-FeMoO₄ would arise from the itinerancy of the *d* electrons caused by the mixed valency.

4. Conclusions

Transition metal molybdates of the formula $A(\text{MoO}_4)_2$ where $A = \text{Fe, Co or Ni}$ exhibit a first order phase transition between 6°K and 9°K. An investigation of the low temperature and high temperature phases by various physical methods including x-ray photoelectron spectroscopy and magnetic susceptibility measurement has revealed that the phase transition is associated with a valence change of the type, $4^{2+} + \text{Mo}^{6+} \rightleftharpoons 4^{3+} + \text{Mo}^{5+}$, at least in the cases of Fe and Co molybdates.

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Enthalpy and entropy changes associated with mixed ligand chelates of Cu(II) and Ni(II) with 4-methoxy picolinic acid N-oxide and some amino acids in aqueous medium

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Abstract. The stability constants of mixed complexes of Cu(II) and Ni(II) with 4-methoxy picolinic acid N-oxide, and glycine, α -alanine, proline and hydroxy-proline have been determined at various temperatures by the potentiometric method in 0.1 M ionic strength. The formation constants of the mixed complexes have been evaluated and are in good agreement with statistically expected values. The enthalpy and entropy values have been calculated from 1:1:1 stability constants temperature coefficient data. From the enthalpy values of the mixed complexes it may be concluded that the bond strengths are not equal to the average of the bond strengths in MA_2 and MB_2 type parent complexes. The entropy values have been found to be favourable for ternary complex formation.

Keywords. 4-methoxy picolinic acid N-oxide; amino acids; mixed ligand complexes; formation constants; thermodynamic parameters.

1. Introduction

The study of formation of ternary complexes of picolinic acid N-oxide (PicO) and some amino acids with Cu(II) have been reported earlier (Sarala Devi and Ram Reddy 1986). In this paper we present the formation constants of Cu(II) and Ni(II) ternary complexes employing 4-methoxy PicO as primary ligand and glycine, alanine, proline and hydroxy proline as secondary ligands. Formation constants were determined by potentiometric methods and calculated with known equations (Ramamoorthy and Santappa 1971; Singh and Srivastava 1973). The proton-ligand and metal-ligand stability constants of binary systems were calculated under the present experimental conditions using the expressions given by Irving and Rossotti (1954) and are presented in table 1. The values thus obtained were found to be in agreement with literature values (Martell and Smith 1971). The enthalpy (ΔH°) and entropy (ΔS°) values associated with above ligands were calculated by known equations and are presented in table 2.

2. Experimental

All the chemicals used were of AR grade. Glycine, α -alanine, proline and hydroxy proline were used as such while 4-methoxy picolinic acid N-oxide was prepared in our laboratory (Ram Reddy *et al* 1981). All solutions were prepared in doubly distilled water. Solutions of Cu(II) and Ni(II) were estimated by titrating with the disodium salt

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Table 1. Stability constants of binary and ternary complexes at 30°C and 0.1 M ionic strength.

	log <i>K</i>	Δ log <i>K</i>	log <i>X</i>
<i>Cu(II) complexes</i>			
4-OCH ₃ PicO	3.94		
Gly	8.27	-1.10	0.53
4-OCH ₃ PicO-Gly	7.17		
Ala	8.15	-1.26	0.12
4-OCH ₃ PicO-ala	6.89		
Pro	8.69	-0.85	0.54
4-OCH ₃ PicO-pro	7.84		
Hpro	8.50	-1.05	0.52
4-OCH ₃ PicO-hpro	7.45		
<i>Ni(II) complexes</i>			
4-OCH ₃ PicO	3.10		
Gly	5.81	-0.21	1.21
4-OCH ₃ PicO-gly	5.60		
Ala	5.35	-0.24	1.02
4-OCH ₃ PicO-ala	5.11		
Pro	6.23	-0.38	0.76
4-OCH ₃ PicO-pro	5.85		
Hpro	6.11	-0.31	1.04
4-OCH ₃ PicO-hpro	5.80		

Table 2. Thermodynamic parameters of binary and ternary complexes at 0.1 M ionic strength.

	-Δ <i>H</i> [‡] kJ mole ⁻¹	-Δ <i>G</i> [‡] (30°C) kJ mole ⁻¹	-Δ <i>S</i> ₁₁₁ [‡] (30°C) JK ⁻¹ mole ⁻¹	-Δ <i>H</i> ₁₁₁ [‡]	Δ <i>S</i> ₁₁₁ [‡]
<i>Cu(II) complexes</i>					
4-OCH ₃ PicO	22.02	22.87	2.80		
Gly	25.53	47.99	94.12	42.91	51.30
4-OCH ₃ PicO-gly	29.05	41.61	41.46		
Ala	18.20	47.30	96.03	41.89	52.57
4-OCH ₃ PicO-ala	25.43	39.96	47.97		
Pro	18.41	50.43	105.67	43.45	62.08
4-OCH ₃ PicO-pro	18.74	45.43	88.31		
Hpro	35.91	49.33	46.94	47.75	39.45
4-OCH ₃ PicO-hpro	37.49	32.50	18.94		
<i>Ni(II) complexes</i>					
4-OCH ₃ PicO	29.05	17.80	-37.14		
Gly	17.15	33.68	54.51	42.41	16.06
4-OCH ₃ PicO-gly	23.43	32.50	29.93		
Ala	11.46	31.00	64.47	38.37	21.80
4-OCH ₃ PicO-ala	16.87	29.68	42.17		
Pro	12.42	35.64	62.59	38.61	34.18
4-OCH ₃ PicO-pro	18.02	33.95	52.57		
Hpro	19.56	35.43	52.37	43.51	17.97
4-OCH ₃ PicO-hpro	28.10	33.66	18.31		

against standard potassium hydroxide at 30°, 40°, 50°C containing (i) acid (4×10^{-3} M); (ii) primary ligand (2×10^{-3} M); (iii) metal nitrate (2×10^{-3} M) and primary ligand; (iv) secondary ligand (2×10^{-3} M); (v) metal nitrate and secondary ligand; (vi) metal nitrate, primary ligand and secondary ligand. The ionic strength was maintained at 0.1 M by adding KNO_3 . All titrations were performed under nitrogen atmosphere. The metal:ligand:ligand ratio was maintained as 1:1:1.

3. Results and discussion

The mixed ligand titration curves of M (II)-4-methoxy PicO ($M = \text{Cu(II)}, \text{Ni(II)}$) with glycine alanine, proline and hydroxy proline at 30°C gave an inflection at $m = 4$ (m refers to moles of base added per mole of metal ion) corresponding to the formation of a ternary complex. These curves were superimposable on the previous 1:1 Cu(II)-4-methoxy PicO and 1:1 Ni(II)-4-methoxy PicO curves respectively upto $m = 3$. This was indicative of 4-methoxy PicO acting as the primary ligand. Similar titration curves were obtained at 40°C and 50°C also indicating the formation of a ternary complex from normal 1:1 M (II)-4-methoxy PicO complex in a stepwise manner. This was further confirmed by a shift of the pH of precipitation in ternary systems compared to binary systems. The data in table 1 show that the stability constants of ternary complexes are lower than those of the 1:1 binary systems of secondary ligand. This can be attributed to the lesser tendency of secondary ligand towards formation of $(MA)^+$ (A is the primary ligand) as compared to that towards formation of $M(\text{H}_2\text{O})_n^{2+}$.

There are two common ways of expressing the stability of ternary complexes: (i) the one approach is based on the disproportionation constant (X), which may be defined as:

$$\log X = 2 \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB})$$

The data in table 1 show that the $\log X$ values are in good agreement with statistically expected values;

(ii) the other approach compares the difference in the stability constants of binary and ternary systems:

$$\Delta \log K = \log K_{MAB}^{MA} - \log K_{MB}^M$$

The $\Delta \log K$ values are calculated and presented in table 1. The experimental values are in the range of (-1.0) to (-1.2) and (-0.22) to (-0.44) for Cu-4-methoxy PicO-AA and Ni-4-methoxy PicO-AA respectively, suggesting distorted octahedral and square planar geometries (Sigel 1975) for the same systems. However, these values are lower compared to the $\Delta \log K$ values of M -PicO-AA systems (Sarala Devi and Ram Reddy 1986). This can be attributed to electron donating groups in 4-methoxy PicO, which decreases the π -acceptor capacity of ligand.

The thermodynamic data in table 2 show that the reactions are exothermic and spontaneous in nature as evidenced by the negative values of ΔH° and ΔG° . The enthalpy and entropy values in ternary complexes vary from the binary complexes. The enthalpy (ΔH°) values in M -4-methoxy PicO-AA systems are lower compared to the values in M -PicO-AA systems. This may be due to the greater electrostatic character of

M-AA bonds in *M-PicO-AA* resulting from the higher π -acceptor capacity of PicO as compared to 4-methoxy PicO.

The enthalpy and entropy changes of the mixed ligand complexes are calculated according to statistical considerations by the following equations (Gergely and Sovago 1973):

$$\Delta H_{111}^x = 1/2 (\Delta H_{12}^A + \Delta H_{12}^B),$$

$$\Delta S_{111}^x = 1/2 (\Delta S_{12}^A + \Delta S_{12}^B) + 4.574 \log 2,$$

and the data is listed in table 2. The enthalpy change ΔH_{111} and entropy change ΔS_{111} accompanying the mixed complex formation are smaller than the statistical values ΔH_{111}^x and ΔS_{111}^x respectively. This can be attributed to factors like the π -acceptor property of ligands, and the electrostatic character of metal ligand bonds. Hence, the strength of the metal ligand bonds in mixed complexes are not equal to the average bond strength in parent complexes.

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Kinetics and mechanism of oxidation of $S_2O_3^{2-}$ by potassium bis(tellurato) cuprate(III)

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Abstract. The kinetics of oxidation of sodium thiosulphate by potassium *bis*(tellurato) cuprate(III) in an alkaline medium has been reported. The reaction is first order in $[S_2O_3^{2-}]$ but zero order in copper(III). Hydroxide ions are found to retard the oxidation rate. A rate expression rationalising the kinetic data has been derived. Sodium tetrathionate has been found to be the product of oxidation.

Keywords. Potassium *bis*(tellurato) cuprate(III); oxidation, thiosulphate; kinetics.

Introduction

Several complexes of copper(III) have been demonstrated to be efficient oxidants with analytical utility (Malprade 1937; Malatesta 1941; Beck 1950, 1951, 1952, 1953). Recently we reported the kinetics of oxidation of methyl ethyl ketone and cyclohexanone (Panigrahi and Pathy 1984) by potassium *bis*(tellurato) cuprate(III). Here a hydroxo tellurato cuprate(III) species was shown to be the active species. The oxidation of nitrophenols (Panigrahi and Pathy 1985a) on the other hand followed a combined first and second order kinetics with more complicated inverse dependence on $[H^-]$. Strangely, retardation by OH^- was also observed in the oxidation (Panigrahi and Pathy 1985b) of CNS^- by Cu(III). In order to throw further light on the behaviour of Cu(III), we report the results of our studies on the kinetics of oxidation of thiosulphate ion by potassium *bis*(tellurato) cuprate(III).

Experimental

The chemicals used were of either AR or *Pro Analytical* grade. A stock solution of potassium *bis*(tellurato) cuprate(III) was prepared and standardised by the procedure of Chandra and Yadav (1968). The solution was stable when preserved in a refrigerator. An appropriate amount of this stock solution was used to prepare the oxidant for kinetic study. Sodium thiosulphate was prepared afresh each time and standardised against standard iodine solution. A suitable quantity of this solution mixed with an appropriate amount of KOH, potassium tellurate and other salts if necessary, were added and made up in a volumetric flask. Potassium nitrate was used to maintain the ionic strength. Both the solutions were thermostated at $30^\circ C (\pm 0.2^\circ C)$ for one hour before the reaction was commenced. The reaction was followed at 415 nm using a visible spectrophotometer (Zeiss vsu 2P) fitted with a thermostatic cell holder which

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was maintained at the desired temperature by circulation of water from a thermostat. Quartz cells of 10 mm thickness were used to hold the solutions. The hydroxide ion concentration in the reaction mixtures was determined by acidimetry. Hydroxide ion concentration remained constant during the period of the reaction. The self-decomposition of Cu(III) was routinely checked and was found to be negligible. The rate constants reported here are the average of at least three independent runs.

3. Results and discussion

A preliminary screening of a mixture of *bis*(tellurato) cuprate(III) ion with sodium thiosulphate in aqueous solution at room temperature indicated slow disappearance of the reddish brown colour due to Cu(III). The reaction mixture after complete consumption of Cu(III) did not contain any turbidity or precipitate. Experiments carried out to determine the stoichiometry using an excess of thiosulphate over Cu(III) indicated the consumption of one mole of oxidant for each mole of thiosulphate

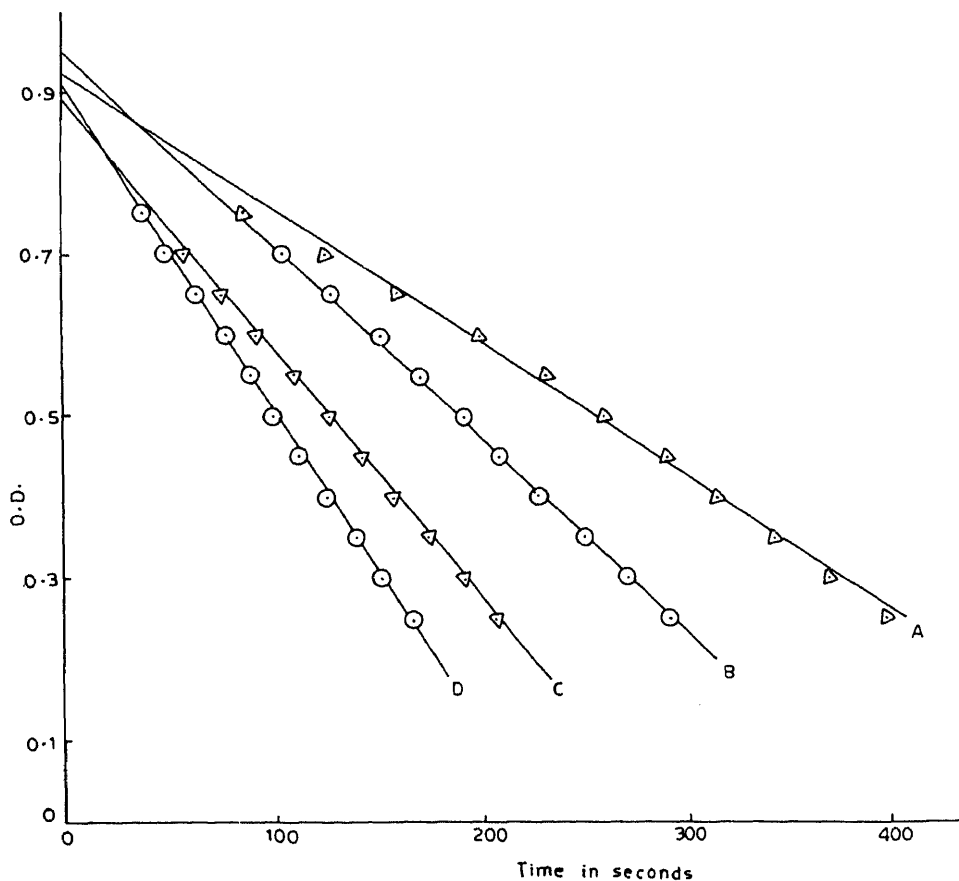
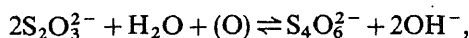


Figure 1. Plot of optical density versus time ($[\text{Cu}^{3+}] = 1.22 \times 10^{-4} \text{ M}$, $[\text{OH}^-] = 1.18 \times 10^{-1} \text{ M}$, $[\text{NO}_3^-] = 1.00 \times 10^{-1} \text{ M}$, $[\text{TeO}_4^{2-}] = 1.0 \times 10^{-1} \text{ M}$, temperature 30°C). (A) $[\text{Sub}] = 0.78 \times 10^{-3} \text{ M}$, (B) $[\text{Sub}] = 1.55 \times 10^{-3} \text{ M}$, (C) $[\text{Sub}] = 1.94 \times 10^{-3} \text{ M}$, (D) $[\text{Sub}] = 2.90 \times 10^{-3} \text{ M}$. (Sub = substrate).

dised,



idently the product of oxidation is tetrathionate when excess of $\text{S}_2\text{O}_3^{2-}$ is used. However, formation of diverse oxidation products like S (Howlett and Wedzicha 1976; nda *et al* 1981), SO_4^{2-} (Deshmukh and Bapat 1957), and S^{2-} (Pryor 1960; Pryor and nellato 1967), in addition to $\text{S}_4\text{O}_6^{2-}$, have been reported with other oxidants.

The kinetics of oxidation of $\text{S}_2\text{O}_3^{2-}$ by potassium bis(tellurato) cuprate(III) in alkaline medium was followed under the conditions of $[\text{S}_2\text{O}_3^{2-}] \gg [\text{Cu(III)}]$ at 415 nm 30°C. The disappearance of Cu(III) was moderately rapid and the plot of absorbance vs time was perfectly linear (figure 1). Such a linearity is consistent with zero order appearance of Cu(III). It is therefore to be concluded that oxidation of $\text{S}_2\text{O}_3^{2-}$ by (III) is kinetically zero order with respect to Cu(III); k_0 was evaluated from the slope the absorbance versus time plot. To confirm zero order dependence with respect to (III), the runs were carried out with varying initial concentrations of Cu(III). It was served that the zero order rate constants are constant within the limits of experimental error. This observation confirms zero order dependence in Cu(III).

Table 1. Average pseudo zero order rate constants for the oxidation of $\text{S}_2\text{O}_3^{2-}$ by potassium bis(tellurato) cuprate(III) in aqueous alkaline medium at 30°C.

$10[\text{OH}^-]\text{M}$	$10^3[\text{Substrate}]\text{M}$	10^3k_0
2.2	1.94	2.40
2.2	2.33	3.13
2.2	2.72	3.57
2.2	3.10	4.00
1.18	0.78	1.60
1.18	1.16	1.94
1.18	1.55	2.39
1.18	1.94	3.00
1.18	2.52	3.50
1.18	2.90	4.50
0.7	0.78	4.78
0.7	1.16	5.08
0.7	1.55	5.58
0.7	1.94	6.07
0.7	2.33	6.90
0.7	2.72	7.68
0.695	1.55	5.06
0.94	1.55	3.82
1.20	1.55	3.5
1.45	1.55	2.97
1.70	1.55	2.5
2.18	1.55	2.13
2.7	1.55	1.66
3.2	1.55	1.52

$[\text{Cu(III)}] = 1.22 \times 10^{-4}\text{M}$, $[\text{TeO}_4^{2-}] = 1.00 \times 10^{-1}\text{M}$

To fix the order with respect to the reductant, namely thiosulphate ion, the kinetics was carried out in the presence of varying initial concentrations of the reductant keeping all other reactants constant. The pseudo zero order constant was observed to increase linearly with increase in thiosulphate concentration (table 1) and the linear plot between k_0 versus $[S_2O_3^{2-}]$ yielded an intercept. Linearity of the above plot suggests first order dependence of the oxidation with respect to $S_2O_3^{2-}$. The plot suggests that the substrate is involved in a hydrolytic equilibrium producing the active species. Further, the slopes are proportional to first order rate constants (k_1) pertaining to oxidation of $S_2O_3^{2-}$. The slopes and intercepts at three different alkali concentrations for $S_2O_3^{2-}$ oxidation are given in table 2.

Table 2. Slopes and intercepts in the plot of [sub] versus oxidation rate under different alkali conditions.

$10 \times [OH^-]$	Slope	Intercept $\times 10^2$
0.7	2	0.24
1.18	1.1	0.065
2.2	1.3	0.00

Sub = substrate.

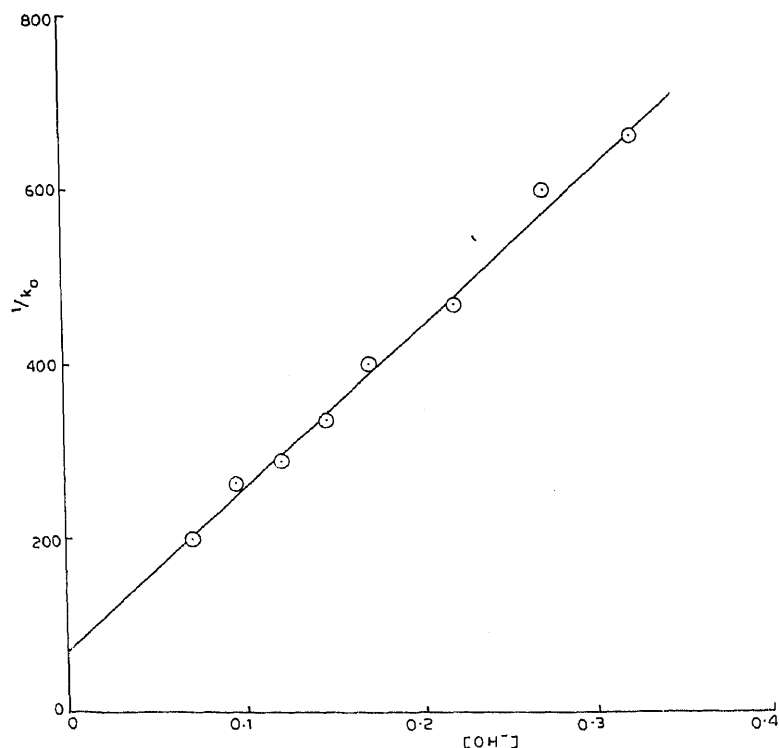


Figure 2. Plot of k_0^{-1} versus $[OH^-]$ ($[Oxid] = 1.22 \times 10^{-4}M$, $[Sub] = 1.55 \times 10^{-3}M$, $[NO_3^-] = 1.00 \times 10^{-1}M$, $[TeO_4^{2-}] = 1.00 \times 10^{-1}M$, temperature $30^\circ C$).

3.1 Effect of added alkali

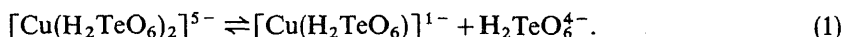
The oxidation of thiosulphate was retarded by increase in alkali concentration and the k_0 values at different NaOH concentrations are included in table 1. Similar observations were also reported by Lee and Lister (1979) in the BrO_2 oxidation of $\text{S}_2\text{O}_3^{2-}$. A plot of k_0^{-1} versus $[\text{NaOH}]$ is linear (figure 2) with an intercept and a positive slope. This observation is consistent with a rate law of the type,

$$k_0^{-1} = a + b[\text{OH}^-],$$

where a and b are terms including the rate constants pertaining to alkali independent and dependent paths.

3.2 Effect of tellurate ion

Unlike oxidation of CNS^- by Cu(III) , the tellurate ion concentration inhibited oxidation till 0.15 M of tellurate ion concentration beyond which the rate was found to be indifferent to further increase of tellurate ion concentration (table 3). Decrease of rate with increase of tellurate ion concentration has been normally attributed to shift in the ionisation equilibria (1) (Movious 1973) to the left since the ditellurato anion is less active than the mono anion species,



In the present study, since Cu(III) is not involved in the rate limiting step, the above explanation seems to be irrelevant, and to explain the observation one has to presume some sort of interaction between $\text{S}_2\text{O}_3^{2-}$ and tellurate ions. It appears that the tellurate ion is able to remove $\text{S}_2\text{O}_3^{2-}$ by complexation forming an inactive species and hence is stable towards Cu(III) . For a given concentration of $\text{S}_2\text{O}_3^{2-}$, after the optimum concentration of tellurate ion is reached, further increase of tellurate ion has practically no effect.

3.3 Salt effect

The k_0 values in the $\text{S}_2\text{O}_3^{2-}$ - Cu(III) reaction were unaffected by added salt concentration which is quite contrary to the CNS^- - Cu(III) reaction (table 4).

Table 3. Average pseudo zero order rate constants for the oxidation of $\text{S}_2\text{O}_3^{2-}$ by potassium bis(tellurato) cuprate(III) in the presence of varying tellurate in an aqueous alkaline medium at 30°C.

$10 \times [\text{TeO}_4^-]$	$k_0 \times 10^{-3}$
0.2	11.87
0.5	4.77
1.0	2.68
1.5	2.13
2.0	2.13
2.5	2.13

$[\text{Cu(III)}] = 1.22 \times 10^{-4} \text{ M}$, $[\text{Sub}]$
 $= 1.55 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 1.44$
 $\times 10^{-1} \text{ M}$, $[\text{NO}_3^-] = 1.00$

Constancy of the zero order rate constants in the presence of varying KNO_3 concentration is self-explanatory since the magnitude of charge does not change as one goes from reactant to activated complex and hence no salt effect or ionic strength effect (Espenson 1981) is observed.

Inspection of the plot (figure 2) of k_0 versus substrate concentration (substrate = sub) at different constant alkali concentrations indicates that the intercept

Table 4. Average pseudo zero order rate constants for the oxidation of $\text{S}_2\text{O}_3^{2-}$ by potassium bis(tellurato) cuprate(III) in the presence of KNO_3 in an aqueous alkaline medium at 30°C .

$[\text{NO}_3^-]$	$k_0 \times 10^{-3}$
0.05	2.5
0.10	2.5
0.15	2.5
0.2	2.5
0.25	2.5

$[\text{Cu(III)}] = 1.22 \times 10^{-4} \text{ M}$, $[\text{Sub}] = 1.55 \times 10^{-3} \text{ M}$, $[\text{TeO}_4^{2-}] = 1.00 \times 10^{-1} \text{ M}$.

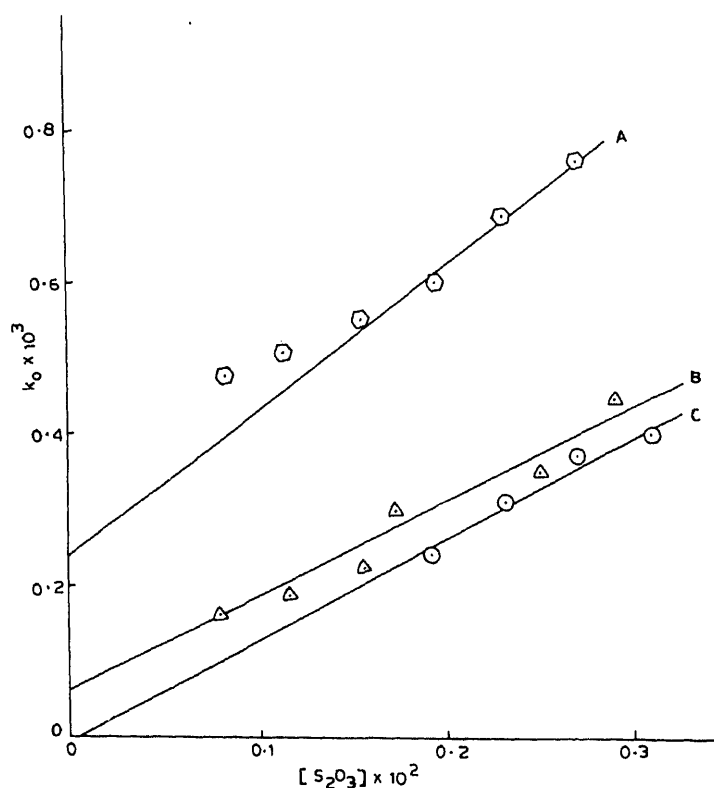
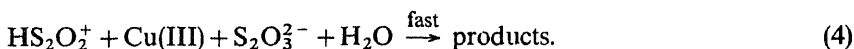
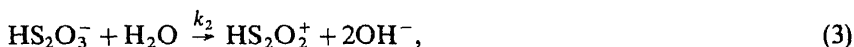
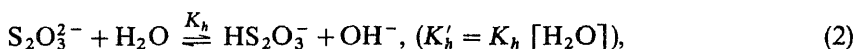


Figure 3. Plot of k_0 versus $[\text{S}_2\text{O}_3^{2-}]$ at different [alkali] ($[\text{Cu}^{3+}] = 1.22 \times 10^{-4} \text{ M}$, $[\text{TeO}_4^{2-}] = 1.00 \times 10^{-1} \text{ M}$, $[\text{NO}_3^-] = 1.00 \times 10^{-1} \text{ M}$, temperature 30°C). (A) $[\text{OH}^-] = 0.7 \times 10^{-1} \text{ M}$, (B) $[\text{OH}^-] = 1.18 \times 10^{-1} \text{ M}$, (C) $[\text{OH}^-] = 2.2 \times 10^{-1} \text{ M}$.

values decrease with increase in alkali concentration. Since intercepts in such plots indicate self decomposition of Cu(III), the higher rate of self decomposition at low alkali concentration is consistent with the greater instability of potassium bis(tellurato) cuprate(III) in low OH^- concentrations. Similarly the slope of the plot at low alkali concentration is quite high compared to that at high alkali concentration indicating that the rate of oxidation of $\text{S}_2\text{O}_3^{2-}$ is higher at low $[\text{OH}^-]$, which is consistent with the decrease of the rate with increase of $[\text{OH}^-]$ (table 2).

In earlier reports of oxidation of $\text{S}_2\text{O}_3^{2-}$ by several metal ions (Beyerley *et al* 1975; Panda *et al* 1982) it has been invariably found to be a case of precursor complex formation between the metal ion and $\text{S}_2\text{O}_3^{2-}$ before the rate limiting decomposition of the precursor complex to products. Recently Panda *et al* (1981), however, had reported zero order dependence with respect to $\text{Fe}(\text{CN})_6^{3-}$ in the oxidation of $\text{S}_2\text{O}_3^{2-}$ in an alkaline medium. In the present investigation also, zero order dependence with respect to Cu(III) rules out participation of the oxidant, either in the rate limiting step or in steps preceding this. Further attempts to detect any precursor complex formation between $\text{S}_2\text{O}_3^{2-}$ and Cu(III) did not succeed.

The observed kinetic data, namely, zero order dependence with respect to the oxidant, retardation of rate by added alkali and indifference of rate to varying ionic strength can be probably rationalised by the following scheme (2-4):



The following rate expression can be derived on the basis of the foregoing steps:

$$-\frac{d[\text{Cu(III)}]_T}{dt} = \frac{k_2 K'_h [\text{S}_2\text{O}_3^{2-}]_T}{K'_h + [\text{OH}^-]}. \quad (5)$$

As the rate expression predicts, the plot of $-d[\text{Cu(III)}]_T/dt$ versus $[\text{S}_2\text{O}_3^{2-}]$ is linear and, $1/d[\text{Cu(III)}]_T/dt$ versus $[\text{OH}^-]$ is also linear, confirming the reaction steps (2)-(4). It is interesting to note that added tellurate retards the rate until an optimum concentration of 0.25 M is reached for a given concentration of Cu(III), unlike in ketone or CNS^- oxidation where no such limiting rate is observed with excess of tellurate. This may probably be due to the formation of a less active thiosulphate species by complexation with tellurate. However, with other substrates involvement of tellurate as a complexing agent is probably ruled out.

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Structure and stability of complexes of thiohydantoin derivative

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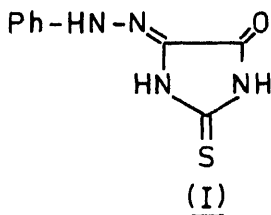
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Abstract. The formation constant of 4-phenylhydrazono-2-thiohydantoin with 3d transition metal ions has been determined. The factors affecting the stability of the metal chelates have been studied. Complexes of Ag(I), Cu(II), Cd(II) and Pd(II) with the ligand have been isolated and characterized by physico-chemical techniques. The ligand forms a 1:1 complex with Ag(I) and 1:2 complexes with the other metal ions.

Keywords. 4-Phenylhydrazono-2-thiohydantoin; transition metal complexes with thiohydantoin; potentiometric studies; IR spectra.

1. Introduction

Many hydantoins have found use in medicine (Ware 1950) first as hypnotics, later for the treatment of chorea, and more recently in the treatment of epilepsy. A variety of hydantoin derivatives are now marketed for more than one medical purpose. However, very little work has been done on the behaviour of these compounds with transition metal ions which commonly exist in biological fluids. As part of our medicinal chemistry programme we recently synthesized new hydantoin derivatives. In this paper we report the measurements of the solution stability of Pd(II), Cd(II), Zn(II), Co(II), Ni(II) and Ag(I) complexes of 4-phenylhydrazono-2-thiohydantoin(**I**). The solid complexes of a few metal ions were isolated and characterized.



2. Experimental

2.1 Materials

Solutions of Pd(II), Cd(II), Co(II), Zn(II), Ni(II) and Ag(I) were prepared in double distilled water from analytical grade palladium chloride, cadmium nitrate, zinc nitrate,

cobalt chloride, nickel chloride and silver nitrate. All solutions were standardized by established procedures (Welcher 1965).

4-phenylhydrazono 2-thiohydantoin(I) was prepared as per Baranov and Perova (1968). All the metal complexes except Ag(I) complex were prepared by mixing 2 m mol of the organic ligand(I) with 1 m mole of the metal ion, both dissolved in the minimum volume of ethanol. Dilute NaOH was slowly added with stirring to adjust the pH of the solution to 7–8, at which the metal chelates precipitate. The complexes were filtered from the solution and then washed thoroughly with an ethanol-water mixture (1:1). The Ag(I) complex was prepared using the ratio 1:1 (Ag:ligand).

EXTCH, model 671 digital pH-meter was used for pH measurements. The pH measurements are devoid of errors arising from solvent and ionic strength of the medium. For this purpose, readings were made on a series of solutions containing known amounts of HCl and NaCl such that μ was 0.1 M. The value of $\log U_H$ in 70% EtOH-water solutions and ionic strength 0.1 M, at 25°C, was found to be -0.25 (Van Uitert and Hass 1953). The IR spectra were recorded (KBr) on a Perkin-Elmer 598 infrared spectrophotometer.

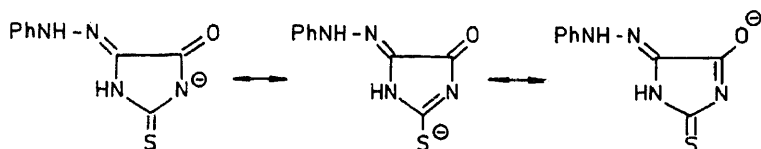
The formation constant determinations were carried out using the following mixtures:

- (i) 5 ml of 1 M sodium chloride + 1 ml of 0.1 M HCl
- (ii) Mixture (i) + 20 ml of 2.5×10^{-3} M ligand
- (iii) Mixture (ii) + 1 ml of 0.01 M metal ion solution.

The total volume of each mixture was made up to 50 ml and at the same time contained 70% in ethanol and had an ionic strength of 0.1 M sodium chloride. The mixtures (40 ml) were separately titrated with a carbonate free 0.05 M NaOH solution. In the case of the Ag(I) complex, the system did not contain HCl solution. The titrations were performed under a purified nitrogen atmosphere and at 25°C. From pH titration curves, the values of $\bar{n}_A$, $\bar{n}$, and pL were calculated as previously reported (Nayan and Dey 1972).

3. Results and discussion

Proton-ligand system: The protonation constant of the thiohydantoin derivative is calculated from the potentiometric titration curves with acid in the presence and the absence of ligand. The formation curve, figure 1, for the proton ligand system was extended between 0 and 1 in the $\bar{n}_A$ scale and it indicated that the ligand has one dissociable proton. The protonation constant $\log K_1^H$ was read directly from the graph. Also, $\log K_1^H$ was calculated by the average value method (Nayan and Dey 1972). Proton release is enhanced by the stability of the conjugate base in which the negative charge can be localised on S, N and O atoms as shown:



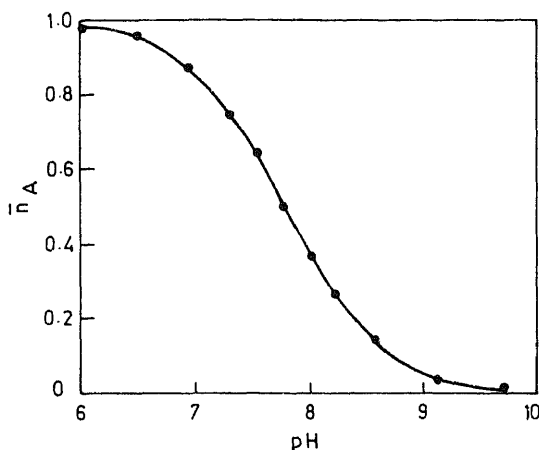


Figure 1. Formation curve for proton-ligand complex of thiohydantoin derivative.

Metal-ligand system: The respective metal ions with the ligand were titrated against NaOH. The metal complex and ligand titration curves are well separated, indicating the liberation of protons due to complexation.

Values of $\bar{n}$ and pL were obtained from previous equations (Nayan and Dey 1972).

$$\bar{n} = [(V''' - V'')(N^0 + E^0)] / [(V^0 + V')T_{CM}^0 \bar{n}_H],$$

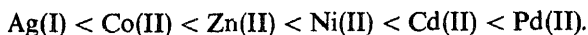
$$pL = \log \{ \beta_n^H [H^+]^n (V^0 + V''') \} / \{ (T_{CL}^0 - \bar{n}T_{CM}^0) V^0 \},$$

where V' , V'' and V''' denote the volume of alkali required to reach the same pH in the titrations of mixture (i), (ii) and (iii) respectively; V^0 the initial volume of the titrated solution; N^0 the normality of alkali; E^0 the initial concentration of the free acid; T_{CM}^0 the total metal ion concentration, T_{CL}^0 the total ligand concentration; and β_n^H the overall proton ligand formation constant value. The graphs of $\bar{n}$ vs. pL , were plotted and are given in figure 2.

The formation curves for metal-ligand complexes show that for Ag(I), the $\bar{n}$ values attain a maximum value of 1, but with other metal ions, it approaches two, thus indicating that with Ag(I) only one complex ML is formed, whereas in other cases two complexes ML and ML_2 are formed stepwise. The values of $\log K_1$ and $\log K_2$ were calculated as previously reported (Nayan and Dey 1972).

The tendency of the metal ion to take up a ligand is proportional to its coordination number. The coordination positions are more freely available for the bonding of the first ligand to a given metal ion than for the second ligand. As such the $\log K_1 - \log K_2$ value is usually positive, based on statistical grounds. In the present study, this value lies within 0.7 to 1.4 $\log K$ units.

It can be seen from the results given in table 1, that $\log K_1$ runs in the order,



The analytical data of the solid complexes, given in table 2, show that the Ag(I) complex has 1 : 1 stoichiometry and the other metal complexes have 1 : 2 stoichiometry.

The IR spectrum of the ligand under investigation show bands occurring at 3170,

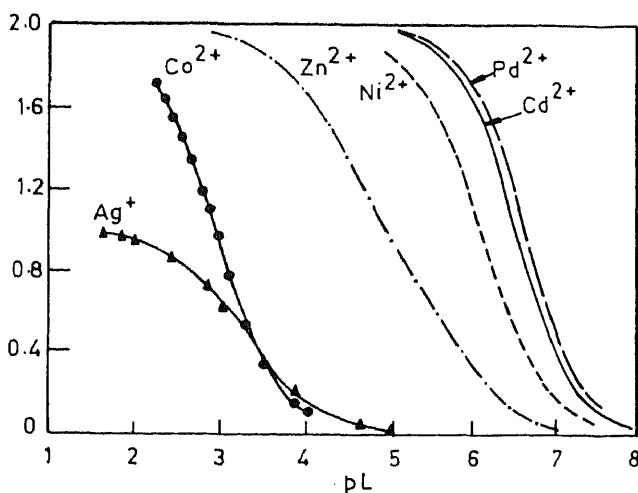


Figure 2. Formation curves for metal complexes of thiohydantoin derivative.

Table 1. Formation constants of some metal ion complexes of the thiohydantoin derivative.

Metal ion	Log K_1	Log K_2	Log β_2
H ⁺	7.65	—	—
Pd(II)	7.00	6.25	13.25
Cd(II)	6.90	6.15	13.05
Zn(II)	5.75	4.35	10.10
Co(II)	3.35	2.55	5.90
Ni(II)	6.55	5.65	12.20
Ag(I)	3.32	—	—

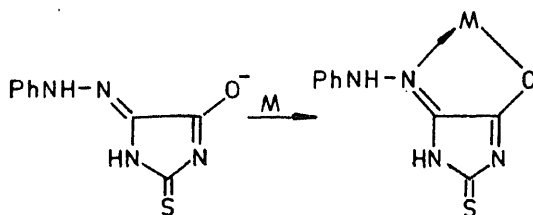
Table 2. Analytical data* of the metal complexes of the thiohydantoin derivative.

Compound	C %	H %	N %	S %	M %
Ag (C ₉ H ₇ N ₄ SO)	33.1 (33.0)	2.2 (2.2)	16.3 (17.1)	9.0 (9.8)	31.9 (32.7)
Cd (C ₉ H ₇ N ₄ SO) ₂	38.9 (39.2)	2.6 (2.6)	19.5 (20.3)	10.7 (11.6)	21.4 (20.4)
Cu (C ₉ H ₇ N ₄ SO) ₂ · 4H ₂ O	37.7 (37.6)	3.9 (3.8)	18.8 (19.5)	10.3 (11.2)	10.9 (11.1)
Pd (C ₉ H ₇ N ₄ SO) ₂ · 3H ₂ O	30.3 (30.9)	3.0 (2.9)	15.2 (16.0)	10.1 (9.2)	14.3 (15.2)

* Calculated values in parentheses.

1700 and 1610 cm^{-1} . These bands may be due to NH, C=O and C=N stretching, respectively (Bellamy 1966). The ligand studied has a thione group (C=S) and protons adjacent to the thione group. It has been stated that the thione group (C=S) is relatively unstable in the monomeric form and tends to turn to a stable =C-SH group, if there is at least one hydrogen atom adjacent to the C=S bond (Mayer 1967). The IR spectrum of the ligand does not display the (S-H) band at 2570 cm^{-1} indicating that, at least in the solid state it remains in the thione form. A medium band at 1370 cm^{-1} in the IR spectrum of the ligand is tentatively assigned as the C=S stretch (Bellamy 1966). Most of the thioureas previously investigated showed a band for the C=S group, occurring in the range $1400\text{--}1500\text{ cm}^{-1}$. This wide range was attributed to varying degrees of coupling as reported by Bellamy.

The IR spectra of Cu(II), Cd(II) and Ag(I) complexes show the disappearance of the NH band. Also, the C=O and C=N absorption bands are red shifted to $\approx 1660\text{ cm}^{-1}$ and $\approx 1580\text{ cm}^{-1}$ respectively. Based on these observations, the complex formation reaction is assumed to occur by the release of a hydrogen ion and participation of carbonyl oxygen together with the C=N group in the formation of a stable five-membered ring as shown in the following. The IR spectrum of the Cu(II) complex shows a broad band occurring at 3450 cm^{-1} which might be due to water molecules.



The IR spectrum of the Pd(II) complex shows the disappearance of $\nu(\text{NH})$ and $\nu(\text{C}=\text{S})$ bands and a blue shift of the carbonyl band to 1720 cm^{-1} . This is explained by the participation of the S-atom and the release of H^+ . The carbonyl oxygen is not involved in complexation.

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Infrared study of $\text{FeO} \cdot \text{OH} \rightarrow \text{Fe}_2\text{O}_3$ thermal transformation

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Abstract. Infrared absorption spectroscopy has been applied for the identification of the minerals associated with natural goethite ($\alpha\text{-FeO} \cdot \text{OH}$) from Saudi Arabia. The thermal transformation of natural goethite as well as the effects of the presence of the associated minerals on the reaction products were investigated. The results revealed that at 300°C protohematite is formed which at 600°C is slightly crystallized. Further recrystallization and hematite formation takes place at 1000°C. It was also found that the presence of other minerals found in goethite samples has no effect on the reaction products.

Keywords. IR; DTA; goethite; thermal transformation.

1. Introduction

It is well known that most of goethites are Al-bearing goethite (Janot *et al* 1970, 1971). The incorporation of Al into goethite structure has been investigated by several authors (Jewur and Kuriacose 1976; Shimokawabe *et al* 1978; Yariv and Mendelovici 1980; Schwertmann *et al* 1977). Schwertmann (1977) stated that dehydroxylation of Al-goethite at 300°C results in poorly crystallized Al-protohematite which at higher temperatures is partly perfected. The difference in the thermal behaviour between pure goethite and Al-bearing goethite is manifested at 600°C when the first is recrystallized, yielding a three-dimensionally ordered structure of hematite; whereas the latter is poorly ordered. Mendelovici and Yariv (1981) investigated the dehydroxylation of natural Al-bearing goethite by IR spectroscopy. They concluded that the spectral features of the iron oxides formed during the thermal treatment depend on the heating temperature, showing that the first dehydroxylation product is Al-bearing protohematite which at temperatures above 600°C is recrystallized to Al-bearing hematite.

The aim of the present study is to apply infrared absorption spectroscopy to investigate the thermal transformation of natural goethite into hematite.

2. Experimental

The samples used in this study were obtained from the collections of the Faculty of Earth Sciences, University of King Abdul Aziz. The localities are Bahra and Wadi Fatimah.

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0.063 mm diameter was selected. Portions of the samples were shaken with 1 N of NaOH solution at 75°C for 10 hours. The powder either in the original form or after a partial removal of associated minerals was heated to different temperatures.

The infrared spectra (IR) were recorded on the PYE UNICAM full automatic double beam spectrophotometer model Sp 3-300. Samples for spectral runs were prepared from finely ground material. For all samples an amount of 3 mg was mixed with 197 mg of KBr and a pellet was made from the mixture.

For thermal analysis DTA instrument (Linsels, selb/Bay) with an automatic strip chart paper recorder was used in the present work to detect the endo- or exothermal reaction changes experienced by the tested samples from room temperature up to 1000°C.

3. Results and discussion

The minerals associated with natural goethite from Bahra and Wadi Fatimah were determined from their IR spectra. The IR spectra of these samples are shown in figures 1 and 2.

As can be seen from figure 1a the spectrum of the sample of Bahra exhibits absorption bands at the frequencies 3125, 890, 790, 660 *sh*, 580, 465 and 410 cm^{-1} . Farmer and Palmieri (1974) pointed out that the absorption of the Fe^{2+} OH ranges from 2900 to 3230 cm^{-1} in goethite and lepidocrosite. The main OH deformation vibrations of Fe^{2+} OH in goethite appear at the frequencies 810 and 910 cm^{-1} (Hartest 1956; Moenke 1962). The infrared spectra of amorphous hydrated iron oxides at the frequencies 3400 *s*, 1630 *w*, 1490 *w*, 1360 *w*, 690 *sh*, 580 *s* and 460 *s* cm^{-1} . Also the spectrum recorded by Estep (1973a) for the amorphous hydrated iron oxide showed

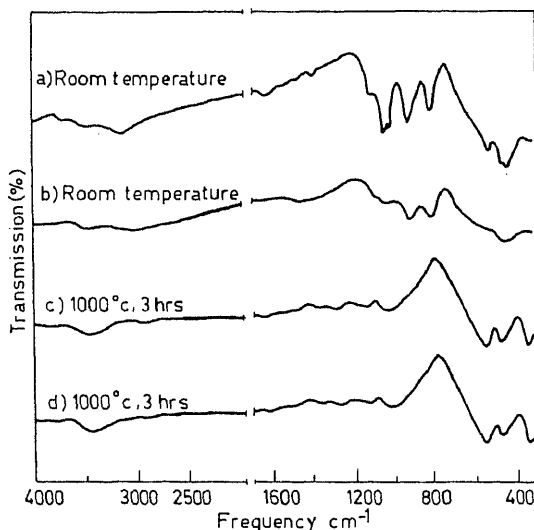


Figure 1.

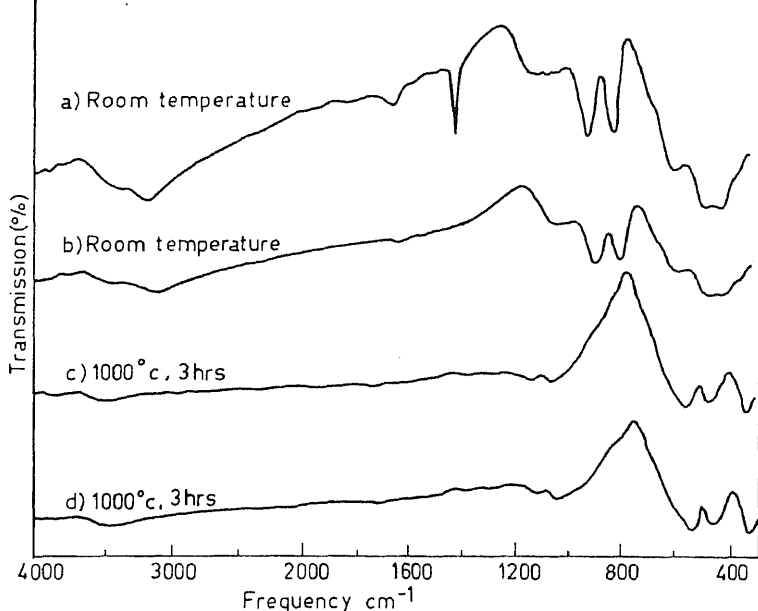


Figure 2.

absorption bands at the frequencies 3400–3390 *s*; 1600 *w*; 1490 *w*; 1370 *w* and 500 *s* cm^{-1} .

In addition to the characteristic bands of goethite the spectrum of the representative sample from Bahra shows a band of medium intensity at 3390 cm^{-1} and very weak absorption bands at the frequencies 1140, 1110, 1080, 1025 and 1000 cm^{-1} . It is unfortunate that the strongest stretching absorption bands of silicate, phosphate, and sulphate anions overlap to a considerable extent in the 1200 to 900 cm^{-1} region. The above absorption bands may be due to the existence of few trace amounts of silicate and sulphate minerals.

The spectrum of the representative sample of Wadi Fatimah in figure 2a is characterized by absorption bands at the frequencies 3110 *w*; 910 *m*; 795 *m*; 590 *sh*; 463 *m*; 437 *m*; and 400 *sh*. cm^{-1} which are the diagnostic frequencies of the mineral goethite (Moenke 1962). Beside these bands other bands occur at the frequencies 3695 *vw*; 3658 *vw*; 3620 *vw*; 3420 *vw*; 1100 *m*; 1028 *m*; 1005 *m*; and 530 *s* cm^{-1} . The structural assignments of these bands were carried out in comparison with literature reports of Alexanian *et al* (1966), Oinuma and Hayashi (1965) and Chester and Elderfield (1973), and with the spectrum of the pure material. It should be mentioned that the absorption bands at 1005, 1028 and 1100 cm^{-1} correspond to the Si-O stretching vibrations of kaolinite (Chester and Elderfield 1973). The absorption bands at 3695, 3658, 3620 and 3420 cm^{-1} are due to the presence of water and hydroxyls in the kaolinite mineral structure (Chester and Elderfield 1973). Accordingly, it could be concluded that kaolinite is associated with the goethite mineral of Wadi Fatimah. The samples from Bahra and Wadi Fatimah are hereafter referred to as goethite (A) and goethite (B) respectively.

It is clear from figures 1a and 2a that the spectral features of minerals associated with goethite (A) are not similar to those associated with goethite (B). The strong band appearing in the spectrum of the former at 580 cm^{-1} appears as a weak shoulder in the spectrum of the latter. In the absorption region from 400 to 500 cm^{-1} the spectrum of goethite (A) shows two absorption bands at 465 and 410 cm^{-1} , whereas the spectrum of goethite (B) shows two medium bands at 463 and 437 cm^{-1} and a shoulder at 400 cm^{-1} . It should be mentioned that the absorption at 463 cm^{-1} has some contribution from kaolinite.

The absorption bands at 3390 , 580 and 465 cm^{-1} are in close agreement with the absorption bands of hydrated iron oxide as reported by Van der Geissen (1968), suggesting that hydrated iron oxide minerals are associated with goethite (A).

In the present study the natural goethites (A) and (B) either in their original forms or after a partial removal of associated minerals were heated to various temperatures and their IR spectra were studied. The removal of part of the associated minerals was carried out by shaking the original ground samples with 1 N NaOH solution at 75°C for 10 hours.

The IR spectra of the original and treated samples after heating to 1000°C are shown in figures 1 and 2 for goethites (A) and (B). The frequencies of the recorded spectra are given in table 1.

It appears from figure 1 curve b that treatment of goethite with the NaOH solution causes no significant changes in the absorption bands of goethite apart from the changes in their intensities. On the other hand, it is clear that this treatment results in remarkable changes in the bands of the associated minerals. The silicate bands appearing in the spectrum of the original sample of goethite (A) at the frequencies 1140 , 1110 , 1080 , 1025 and 1000 cm^{-1} have disappeared from the spectrum of the treated one and the latter spectrum exhibits a broad band at 1035 cm^{-1} with a shoulder at 1070 cm^{-1} . Also, the kaolinite bands appearing in the spectrum of the original goethite (B) in figure 2 curve a at 3695 , 3658 , 3620 , 3420 , 1100 , 1028 , 1005 and 530 cm^{-1} are

Table 1. Frequencies of O^{2-} displacements in hematite obtained after calcination of goethite (A) and goethite (B).

Heating temperature ($^\circ\text{C}$)	Goethite (A)		Goethite (B)	
	Original sample	NaOH treated	Original sample	NaOH treated
300	328	325	318	318
	450	450	448	448
	525	530	532	535
	550 sh	550 sh		
600	330	330	313	312
	460	453	450	445
	540	540	533	532
	560 sh	560 sh		
1000	332	335	331	333
	467	468	475	470
	547	545	548	550

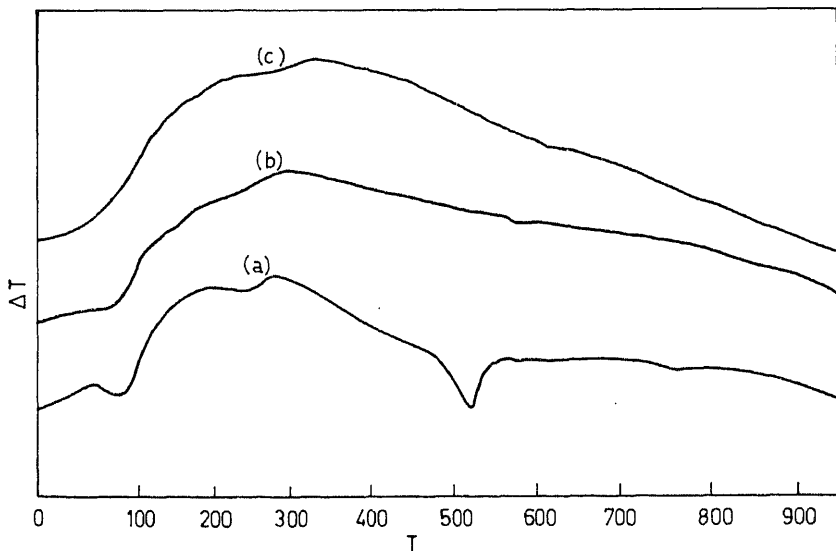
absent from the spectrum of the treated sample (figure 2 curve b). The spectrum of this treated sample shows a broad band at 1020 cm^{-1} and a shoulder at 1070 cm^{-1} .

The frequencies of goethites (A) and (B) after heating at temperatures 300°C and 600°C for 24 hours and at 1000°C for 3 hours are given in table 1. Examination of the recorded spectra of the heated samples revealed that the spectrum of the sample heated at 300°C is characterized by three broad absorption bands at 525 , 450 and 328 cm^{-1} and a strong shoulder at 550 cm^{-1} which are assigned as O^{2-} displacement. These bands shift to 540 , 460 and 330 cm^{-1} and to 547 , 467 and 332 cm^{-1} with temperature increasing to 600°C and 1000°C respectively. Also, it is evident from figure 1 that the bands become narrower with increasing temperature. Parallel changes were recorded during thermal treatment of samples treated with NaOH solution.

The spectrum of the sample of goethite (B) heated at 300°C exhibits the main three bands at frequencies 532 , 448 and 318 cm^{-1} . These bands occur at frequencies 533 , 450 and 313 cm^{-1} in the spectrum of the sample heated at 600°C and at frequencies 548 , 475 and 331 cm^{-1} in the spectrum of the sample heated at 1000°C . Figure 2 reveals also that the thermal behaviour of the sample treated with NaOH solution is similar to that of the original sample.

Mendelovici and Yariv (1981) mention that the band at about 540 cm^{-1} is highly sensitive to both factors (1) the heating temperature of the laterite samples, and (2) the initial gibbsite content. However, the IR spectra of the analyzed samples reveal that they are nearly free of gibbsite and contain considerable amounts of aluminium silicate minerals. Although the existence of these minerals is associated with natural goethite, the shifts in the peak maxima of the bands at 535 , 465 and 325 cm^{-1} are in good correlation with those reported in the literature for pure goethite (Mendelovici and Yariv 1981; Yariv and Mendelovici 1979).

Figure 3 illustrates the DTA curves of goethite (B) after heating at 300 , 600 and 1000°C . In figure 3 curve a the endothermic peak at 75°C is due to absorbed water but



the small endothermic peak at 250–280°C is due to partial transformation of goethite to hematite (Todor 1976), which is not clear in the samples preheated at 600 and 1000°C, thus proving the complete transformation of goethite to hematite after firing at 600 or 1000°C.

The very clear endothermic peak at 525°C is due to the removal of the hydroxyl groups of kaolinite present with the goethite, which disappears by preheating at 600 and 1000°C as shown in figure 3 curves b and c.

The very small peak at 575°C, which is characteristic of the α - β quartz transformation, proves the presence of very small amounts of free silica with the goethite which is found to be repeated in the three samples owing to the fact that this transformation of the quartz modifications is a reversible one.

The above results lead to the conclusion that at 300°C protohematite is formed which at 600°C is slightly crystallized. Further recrystallization and hematite formation occurs at 1000°C. The presence of the various minerals found associated with goethite has no effect on the reaction products.

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Polychalcone derived from 8-acetoxyquinoline-5-aldehyde

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Abstract. Fries rearrangement of 8-acetoxyquinoline-5-aldehyde (AQA) in nitrobenzene using AlCl_3 as catalyst affords the polychalcone poly(8-hydroxy-5,7-quinolinylenecarbonylvinylene) (PHQCV). The PHQCV samples were characterized by elemental analysis, IR spectroscopy, molecular weight, intrinsic viscosity and TGA.

Polymeric metal chelates of Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} and UO_2^{2+} with PHQCV polychalcone were prepared and characterized.

Keywords. 8-Acetoxyquinoline-5-aldehyde; polychalcone; poly(8-hydroxy-5,7-quinolinylenecarbonylvinylene); polychelates of polychalcone; poly(8-hydroxy-5,7-quinolinylenecarbonylvinylene)-metal.

Introduction

Sessel (1948) has reported that Fries rearrangement (FR) of 4-acetoxybenzaldehyde affords the polymeric product containing chalcone groups in the polymer chains. Because of the good chelating properties of polymers prepared from 8-hydroxyquinoline (8HQ) (Harrison and Williams 1959; Vernon and Nyo 1978; Patel and Patel (1979); Patel and Patel (1984) and because of polymers based on the FR of 8-acetoxyquinoline-5-aldehyde (AQA) have not been reported so far, it was considered interesting to prepare such polymers to study their chelating properties. The work in the present communication is connected with the synthesis, characterization and chelation with metal ions of poly(8-hydroxy-5,7-quinolinylenecarbonylvinylene) (PHQCV).

Experimental

Materials and methods

8-Hydroxyquinoline-5-aldehyde (HQA) was prepared by a method reported earlier (Sen and Ray 1932). 8-Acetoxyquinoline-5-aldehyde (AQA) was prepared by acetylation of HQA with excess of acetic anhydride in pyridine. All other chemicals used were of analytical grade.

Preparation of polychalcone (PHQCV) by Fries rearrangement of AQA: To a well stirred and ice-cooled solution of AQA (0.1 mol), finely powdered anhydrous aluminium chloride (0.2 mol) in nitrobenzene (6.0 ml) was added in small portions. The reaction mixture was allowed to come to room temperature and then heated to 100°C for 3 hr and further to $120\text{--}130^\circ\text{C}$ for 10 hr. The resultant dark green viscous reaction mixture was poured into ice cooled dilute HCl (500 ml, 5%). Nitrobenzene was removed by steam distillation and the green solid was collected and air dried. It was Soxhlet-

2.1b Preparation of polymeric chelates of *PHQCV* polychalcone *Preparation of *PHQCV*-Cu²⁺ chelate* To a solution of copper nitrate (0.01 mol) in 40 ml of a formic acid (60% v/v), a solution of *PHQCV* (0.01 mol) in 40 ml of formic acid (85% w/v) at room temperature was added dropwise, with good stirring. The mixture was then heated on a water-bath for 1 hr. The pH was adjusted to the required value (4.5) by the addition of dilute ammonia solution when the polymeric chelate separated out in the form of a suspension. The latter was digested for 1 hr on a water-bath and collected by decantation. The polymeric chelate was filtered, washed with ethanol and then air dried. It was designated as *PHQCV*-Cu²⁺.

Following this method other metal chelates listed in table I were prepared.

3. Analyses of *PHQCV* polychalcones and polymeric chelates

(a) The nitrogen contents in the *PHQCV* polychalcone samples and the other polymeric chelates were estimated by Dumas' method. The analyses of metal ions in the polymeric chelates were carried out by the decomposition of a known amount of chelate with mineral acids. The metal content was estimated by a method reported in literature (Vogel 1979).

(b) The IR spectra of *PHQCV* polymer and polymeric metal chelates were scanned as pellets on a Perkin-Elmer 983 Spectrophotometer.

(c) Conductometric titration of *PHQCV* polymer sample was carried out in pyridine against sodium methoxide (NaOMe) in pyridine as standard. The value of the theoretical average molecular weight (M_n) was calculated following a method of conductometric titration reported by Chatterjee (1971).

(d) Intrinsic viscosity $[\eta]$ of the *PHQCV* polymer sample was estimated in 85% formic acid-acetic acid mixture at 30 ± 0.1°C. Ubbelohde viscometer was used for this purpose.

(e) Thermogravimetry of the *PHQCV* polymer sample and all polymeric chelates were carried out on Linseis thermobalance at a heating rate of 10°C/min.

4. Results and discussions

4.1 Characterization of the polychalcone *PHQCV*

Fries rearrangement (FR) of 8-acetoxyquinoline-5-aldehyde (AQA) was carried out in nitrobenzene by varying temperature and the molar proportion of AlCl₃. It was observed that the FR of AQA could not be effected below 100°C but only above 120°C. It was also observed that more than 2 mol of AlCl₃ yield a polymer which could not be isolated. This is because of the requirement of higher concentration of HCl for the decomposition of more AlCl₃ which simultaneously dissolved the polymeric product.

The *PHQCV* polymer sample was in the form of green powder, did not melt up to 300°C and was insoluble in common organic solvents. It was soluble only in formic acid and HCl. The

Table 1. Characterization of PHQCV polychalcone and its metal chelates.

Polymer chelate	Molecular weight of repeating unit (g/mol.)	Metal content %		Nitrogen content %		Weight loss at various temperature (%)					
		Calcd.	Found	Calcd.	Found	200°C	300°C	400°C	500°C	600°C	700°C
PHQCV-Cu ²⁺	455.54	13.94	13.5	6.15	5.8	3	12	30	40	75	95
PHQCV-Fe ³⁺	644.84	8.66	8.41	6.51	6.3	4	12	32	41	73	95
PHQCV-Co ²⁺	450.93	13.07	12.75	6.2	5.7	3	14	35	58	76	95
PHQCV-Zn ²⁺	457.38	14.37	13.95	6.12	5.7	2	11	28	70	78	95
PHQCV-Mn ²⁺	446.93	12.3	12.00	6.26	5.9	2	15	30	68	80	98
PHQCV-Ni ²⁺	450.71	13.03	12.68	6.21	5.6	3	15	35	65	80	95
PHQCV-UO ₂ ²⁺	662	35.95	34.5	4.23	3.8	6	8	40	55	65	85

Analysis of PHQCV polychalcone: Mol. wt. of repeat unit: 192; N %: Calcd. 6.79; Found. 5.95, $\bar{M}_n$: 1035 $\pm$ 40; $[\eta]$ in formic acid-acetic acid (85/15, v/v); mixture: 4.15 dl g⁻¹; Wt. loss at various temp. (%): 3 (300°C), 20 (400°C), 60 (500°C), 78 (660°C) 95 (700°C).

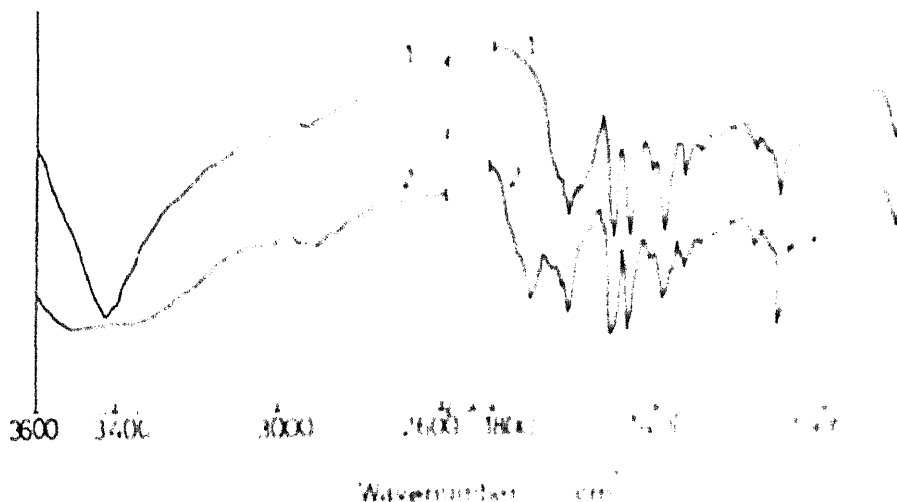


Figure 1. IR Spectra of 1 mg of polychalcone (2 mg of 2,6-dimethyl-4-nitrobenzoate).

aromatic C-H stretching vibration. In this region no separate band is observed for ν_{CH} of chalcone group. A broad band around 1680 cm^{-1} may be attributed to $\nu_{\text{C=O}}$.

of conjugated C=C-H-C-H system (Mecke and Noack 1969). The strong bands at 1300 and 1200 cm^{-1} due to $\nu_{\text{C=C}}$ are also observed. However the band due to $\nu_{\text{C=C}}$ could not be discerned distinctly. Hence this was confirmed by bromination of PHQCV polymer. The bromine content of brominated ring is consistent with the presence of chalcone group in the parent polymer chain.

These suggest that the IR of PHQCV may be postulated by the formation of the aldehyde intermediate and its spontaneous self polycondensation via Aldol condensation in an acidic medium to polychalcone PHQCV by the route shown in chart 1.

The number average molecular weight (M_n) (table I) of PHQCV polychalcone determined by conductometric titration was found to be 10^4 . The intrinsic

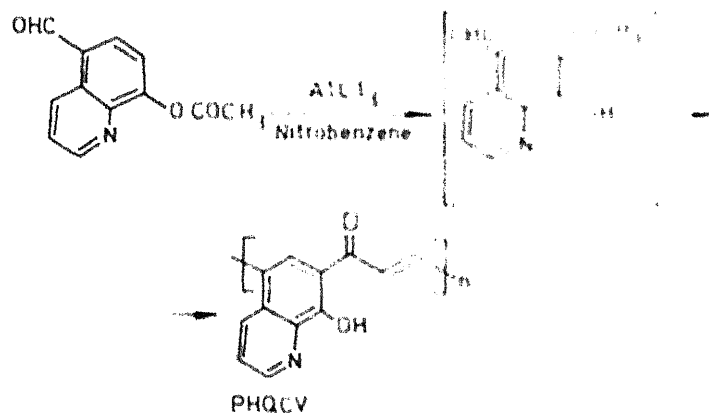


Chart 1.

$[\eta]$ of PAHQ polychalcone in formic acid–acetic acid (85:15, v/v) mixture was found to be 4.15 dl g^{-1} . The results of TG analysis of PHQCV polychalcone show that it starts decomposition at a perceptible rate at some temperature around 300°C . Beyond this temperature the polymer samples degrade very rapidly and loses its weight completely round 700°C . Comparison of the thermal properties of the produced polychalcone with those of polymers derived from 8HQ (Pennington and Williams 1959; Patel and Patel 1979; Patel *et al* 1984) reveals that PHQCV is less stable. This may be due to thermooxidation reactions in the polymer chain which arise due to the dehydrogenation of OH groups (Jackson and Conley 1964) and the formation of the new carbonyl groups of their acidic or quinoid type radicals (chart 2).

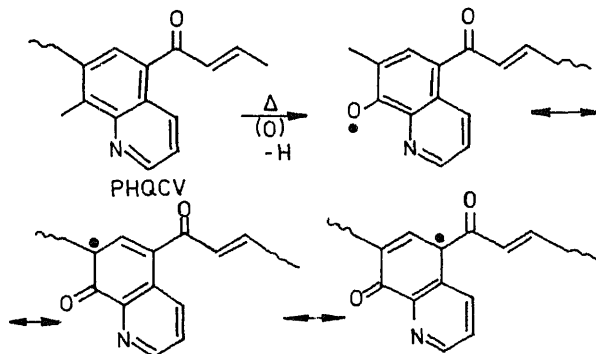


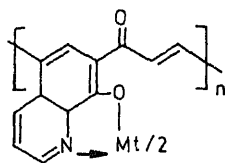
Chart 2.

4.2 Characterization of chelates of PHQCV

All the polymeric chelates presented in table 1 are found to be insoluble in common organic solvents. They did not melt up to 360°C . The results of metal and nitrogen analyses are shown in table 1. The values for the metal contents suggested that the metal:ligand ratio is 1:2 for all bivalent metal ions and 1:3 for Fe^{3+} ions. These results were also supported by nitrogen analyses of polymeric chelates.

The IR spectra of the polymeric chelates resembled each other in their general shape and in the relative intensity of bands. Comparison of the IR spectrum of the polymeric ligand and of the polymeric chelate PHQCV-Cu^{2+} (figure 1) reveals that the broad absorption in the region $3500\text{--}2500 \text{ cm}^{-1}$ in the spectrum of the polymeric ligand, due to chelated OH groups, are much less broad in the spectrum of the polymeric chelate. This indicates the absence of internal H-bonding due to chelation, which is in agreement with the studies of coordination polymers of bis(oxine) (Horowitz and Perros 1964). In the IR spectra of polymeric chelates the band around 1700 cm^{-1} due to $\nu_{\text{C=O}}$ appeared more clearly. Hence, it can be inferred that the carbonyl of the chalcone group could not participate in the chelation. The weak band appearing at 1100 cm^{-1} is attributed to the C–O–M stretching frequency (Charles *et al* 1958). All these features suggest the structure of polychelates is as in chart 3.

Examination of the thermograms and thermal analysis (table 2) of all the polymeric chelates reveals that like PHQCV polychalcone, each polymeric chelate degrade above 300°C . The rate of decomposition of the polymeric chelate is comparatively thermally less stable than PHQCV. It seems that the metal ions accelerate the decomposition of the polymeric chelate (Horowitz and Perros 1964).



Mt: Cu^{2+} , Ni^{2+} , Co^{2+} ,
 Zn^{2+} , Mn^{2+} , UO_2^{2+}

$$\text{Mt} / 3 : \text{Fe}^{3+}$$

Chart 3.

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Anomeric effect in carbohydrates—an *ab initio* study on extended model systems

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Abstract. The anomeric effect is studied at the *ab initio* Hartree-Fock level using extended model systems. This has enabled us to study the effect of substitution on the anomeric effect and the Δ^2 -effect in greater detail. An attempt is made to compare the results with available experimental data.

Keywords. Anomeric effect; carbohydrates; model systems.

1. Introduction

The anomeric effect discovered by Edwards (1955) and Lemieux (1958) and Chu (1958) has gained theoretical support by several *ab initio* studies in the past decade (Wolfe *et al* 1969; Jeffrey *et al* 1972, 1974, 1978; Jeffrey and Yates 1979, 1980, 1981; Schaefer 1981; Vishweshwara and Rao 1982; Allinger 1984). Although there is a general agreement between theory and experiment, certain aspects, like the correlation between the substituent on oxygen at C1 and the anomeric energy (Stoddart 1981), the Δ^2 effect (Reeves 1949; Durette and Harton 1971) which arises due to the axial orientation of the OH group on C2 of a pyranose, are not clear. The anomeric effect is generally recognised as the property of the O5–C1–O1 fragment. However, the experimental results (Reeves 1950; Stoddart 1981) include to some extent, factors like the other intra and intermolecular interactions including the effect of solvents. On the other hand, theoretically, the anomeric effect can be studied as a phenomenon associated only with the (O–C–O) fragment. Hence, related properties, like the *exo*-anomeric effect, the Δ^2 effect and the effect of substitution, can be studied as a perturbation on the (O–C–O) fragment. One can consider a number of model systems with appropriate substituents on the various atoms of methane-diol molecule. In view of this, the systems 1,1-dihydroxyethane, 1,1-dimethoxyethane, 1,1,2-trihydroxyethane and 2,2-dimethoxyethanol are studied at the *ab initio* level. The results obtained, along with those of other previous theoretical studies have been used to analyse the trends in properties associated with the anomeric effect. Also, the results are compared with experimental values whenever possible.

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2.

2.1 Method

The calculations were carried out mainly at the RHF/STO-3G level (Hehre *et al* 1969) using a DEC-10 version of GAUSSIAN 74 (Hehre *et al* 1975). Although, it is desirable that all calculation be carried out at a higher level basis set and with complete geometry optimization, it was not possible to achieve that level of sophistication because of the size of the systems and computer time. However, the conclusions drawn from these studies are valid since on detailed comparison, the present results are in general agreement with the earlier more sophisticated calculations carried out on smaller systems.

2.2 Model systems and geometry

Relevant portions of the carbohydrate moieties have been modelled with smaller molecules. To investigate the anomeric effect in 2-deoxypyranoses and 2-deoxypyranosides, 1,1-dihydroxyethane and 1,1-dimethoxyethane have been taken as model systems respectively (figure 1). To investigate the Δ^2 effect in simple and 1-O-methylpyranosides, 1,1,2-trihydroxyethane and 2,2-dimethoxyethanol (figure 2) have been considered as model systems respectively.

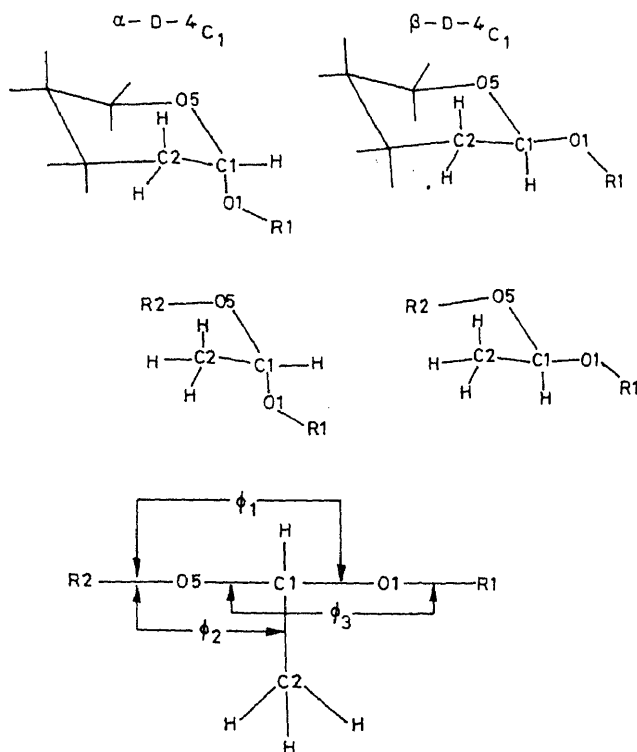


Figure 1. Relation between conformations of 2-deoxy pyranoses and 1,1-dihydroxyethane ($R_1 = R_2 = H$); and 2-deoxypyranosides and 1,1-dimethoxyethane ($R_1 = R_2 = CH_3$).

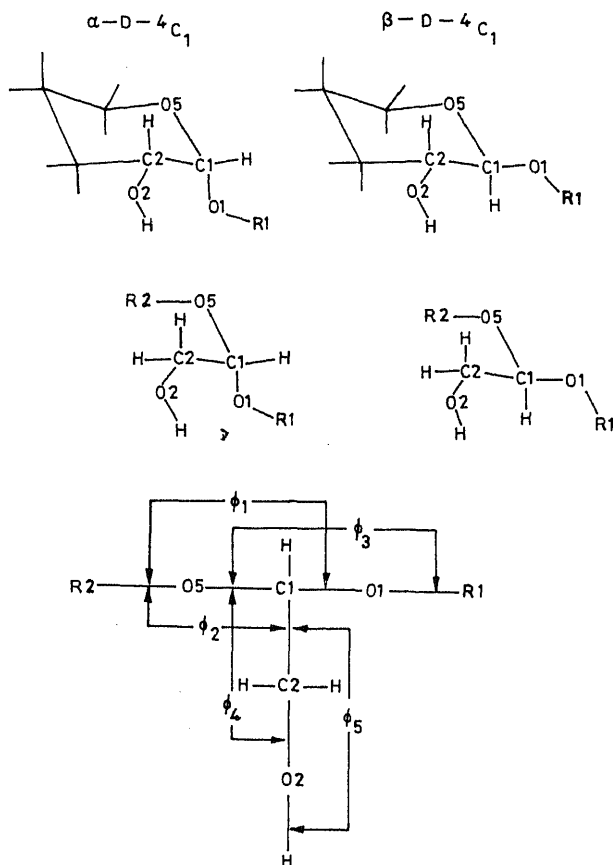


Figure 2. Relation between conformations of pyranoses and 1,1,2-trihydroxyethane ($R_1 = R_2 = H$); and pyranosides and 2,2-dimethoxyethanol ($R_1 = R_2 = CH_3$) (OH at C2 is axial for mannose-like pyranoses and pyranosides).

Standard values of bond lengths (Pople and Gordon 1967) ($C-C = 1.54$ Å, $C-O = 1.43$ Å, $C-H = 1.09$ Å, $O-H = 0.96$ Å) and tetrahedral valence angles were used to fix the various atoms in these molecules. Corresponding to a model for α -D-4C₁ configuration of a pyranose or a pyranoside the dihedral angles ϕ_1 and ϕ_2 were fixed at 60° and -60° respectively. For β -D-4C₁ configuration the dihedral angles were fixed as $\phi_1 = 180^\circ$ and $\phi_2 = -60^\circ$. For 1,1,2-trihydroxyethane and 2,2-dimethoxyethanol values of ϕ_4 of 180° and -60° describe the equatorial and axial disposition of C2 hydroxyls respectively.

By varying the dihedral angle ϕ_3 in steps of 60° energies were computed in each case for 1,1-dihydroxyethane and 1,1-dimethoxyethane. Calculations were repeated for 1,1-dimethoxyethane using the available optimized angles for dimethoxymethane (Gorenstein *et al* 1977). In the case of 1,1,2-trihydroxyethane and 2,2-dimethoxyethanol energies were computed by varying the dihedral angles ϕ_3 and ϕ_4 after fixing ϕ_1 , ϕ_2 and ϕ_5 at respective values corresponding to the model

for α -D- 4C_1 or β -D- 4C_1 configuration for both axial and equatorial orientations of C2-OH bond.

3. Results

3.1 1,1-dihydroxyethane

The energies for 1,1-dihydroxyethane computed as a function of ϕ_3 after fixing the other dihedral angles at values mentioned in §2.2 are given in table 1. The table shows that the minimum occurs at $\phi_3 = 60^\circ$ and -60° corresponding to the α -D- 4C_1 and β -D- 4C_1 configurations respectively. However, the minimum for the β -D- 4C_1 configuration is about 2.5 kcal mol $^{-1}$ higher in energy than that for the α -D- 4C_1 configuration. This difference represents the anomeric energy and is slightly higher than the value (2.24 kcal mol $^{-1}$) obtained using methanediol (Vishweshwara and Rao 1982) as a model system. However, the 4-31G value is 4.7 kcal mol $^{-1}$ (Jeffrey *et al* 1972). It is interesting to note from the table and figure 3 that for β -D- 4C_1 configuration ϕ_3 favours -60° over 60° by about 0.6 kcal mol $^{-1}$ and the conformation with $\phi_3 = 0^\circ$ is almost of equal energy as the one with $\phi_3 = 60^\circ$. Such a preferred eclipsed conformation was also found in methanediol (Jeffrey *et al* 1972) and this is due to favourable dipolar interaction in the conformation with $\phi_3 = 0^\circ$.

In the β -D- 4C_1 configuration, the distinction between $\phi_3 = -60^\circ$ and $+60^\circ$ was not possible using methanediol as a model system. However, the difference in the energy between these two conformations cannot be considered as *exo*-anomeric energy (as defined by Jeffrey and Yates 1981) since in this case it arises purely due to steric reasons and the interaction of bond dipoles and lone pairs on oxygen of the -O-C-O- fragment is identical in both $\phi_3 = -60^\circ$ and $+60^\circ$ conformations. The calculated *exo*-anomeric energies (the energy difference between $(\phi_1, \phi_3) = (60^\circ, 180^\circ)$ and $(60^\circ, 60^\circ)$ conform-

Table 1. STO-3G conformational energies of 1,1-dihydroxyethane.

Configuration ^a	ϕ_3 (degree)	Relative energy (kcal mol $^{-1}$)
α -D- 4C_1	0	3.69
	60	0.00 ^b
	120	2.46
	180	3.08
	-120	3.96
	-60	3.15
β -D- 4C_1	0	3.05
	60	3.08
	120	6.93
	180	7.50
	-120	6.26
	-60	2.49

^a For α -D- 4C_1 configuration, $(\phi_1, \phi_2) = (60^\circ, -60^\circ)$; for β -D- 4C_1 configuration, $(\phi_1, \phi_2) = (180^\circ, -60^\circ)$.

^b Total energy = -225.9693089 hartrees.

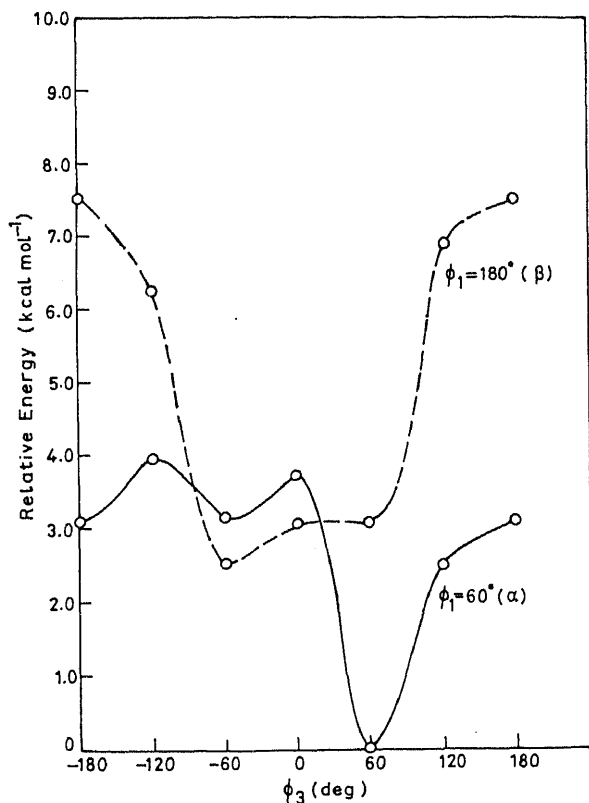


Figure 3. Relative energies drawn as a function of ϕ_3 for internal rotation in 1,1-dihydroxyethane, for fixed values of ϕ_1 .

s for α -D-⁴C₁ and that between (180°, 180°) and (180°, -60°) conformations for ⁴C₁ configurations) are 3.08 and 5.01 kcal mol⁻¹ for the α -D-⁴C₁ and β -D-⁴C₁ configurations respectively. The increased *exo*-anomeric energy as compared to that in anediol is due to the added steric interaction between the -CH₃ group on C1 and proton on O1 in (60°, 180°) and (180°, 180°) conformations respectively in α -D-⁴C₁ β -D-⁴C₁ models.

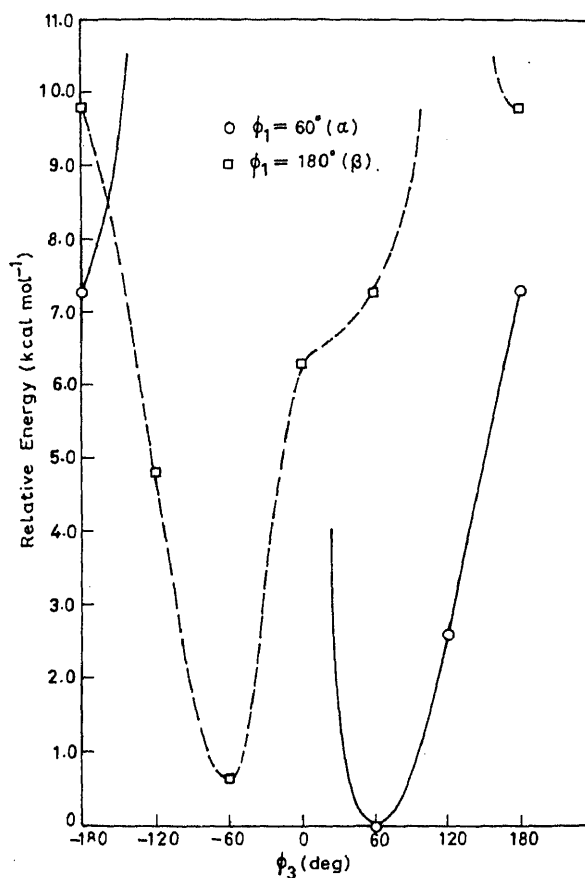
1,1-dimethoxyethane

computed energies of 1,1-dimethoxyethane are given in table 2. The variation of energy with ϕ_3 is shown in figure 4. The lowest energy configuration is again equivalent to α -D-⁴C₁ and is favoured by about 0.6 kcal mol⁻¹ over the β -D-⁴C₁. The energy difference between α and β configurations is small (0.6 kcal mol⁻¹) when compared to (2.5 kcal mol⁻¹) in 1,1-dihydroxyethane, suggesting that a methoxyl substituent at carbon reduces the anomeric energy significantly. The *exo*-anomeric energies are 9.20 and 9.20 kcal mol⁻¹ respectively for the α -D-⁴C₁ and β -D-⁴C₁ configurations, and the increase in *exo*-anomeric energy is due to increased steric effects between the -CH₃ groups on O1 and C1 in (ϕ_1, ϕ_3) = (60°, 180°) and (180°, 180°) conformations. It thus

Table 2. sro-3G conformational energies of 1,1-dimethoxyethane.

Configuration ^a	ϕ_3 (deg.)	Relative energy (kcal mol ⁻¹)	
		Standard geometry	Optimized geometry
α -D- ⁴ C ₁	0	217.70	
	60	0.00 ^b	-1.02
	120	2.60	
	180	7.24	
	-120	22.95	
	-60	224.20	
β -D- ⁴ C ₁	0	6.29	
	60	7.24	
	120	23.72	
	180	9.81	
	-120	4.79	
	-60	0.61	-0.44

^a as in table 1; ^b total energy = -303.1273774 hartrees.

**Figure 4.** Relative energies drawn as a function of ϕ_3 for internal rotation in 1,1-

seems that a methoxyl substituent at the C1 carbon reduces the anomeric energy and increases the *exo*-anomeric energy. The energies obtained using the STO-3G optimized bond angles of dimethoxymethane (Gorenstein *et al* 1977) also lead to the same value for the anomeric energy (table 2).

3.3 1,1,2-Trihydroxyethane

In this system corresponding to a model for α -D- 4 C₁ and β -D- 4 C₁ configurations $\phi_4 = 180^\circ$ and -60° represent the equatorial and axial orientations of C2-OH group respectively as mentioned in § 2. Energies were calculated as a function of ϕ_3 by fixing ϕ_5 (figure 2) in all the three staggered orientations and the values are given in table 3. The minimum energy conformation ($\phi_3, \phi_5 = 60^\circ, -60^\circ$) for α -D- 4 C₁ configuration when C2-OH is equatorially oriented, has about 2.2 kcal mol⁻¹ lower energy than the β -D- 4 C₁ configuration ($\phi_3, \phi_5 = -60^\circ, 60^\circ$) and this is the anomeric energy. On the other hand, when the hydroxyl group at C2 is axially oriented the anomeric energy is 2.4 kcal mol⁻¹. The calculated *exo*-anomeric energies (the energy difference between (ϕ_1, ϕ_3) = (60°, 180°) and (60°, 60°) conformations for α -D- 4 C₁ and that between (180°, 180°) and (180°, -60°) conformations) for β -D- 4 C₁ configurations, with the lowest

Table 3. STO-3G conformational energies of 1,1,2-trihydroxyethane.

Configuration ^a	ϕ_4	ϕ_3	ϕ_5		
			60	180	-60
α -D- 4 C ₁	180 (C2-OH equatorial)	0	6.14	5.85	3.70
		60	2.60	2.00	0.00 ^b
		120	4.67	3.27	2.34
		180	3.58	2.12	6.09
		-120	4.08	4.06	7.70
		-60	5.07	5.00	3.81
β -D- 4 C ₁		0	2.70	5.12	5.49
		60	3.44	4.85	5.00
		120	10.41	6.91	7.04
		180	10.21	6.41	8.00
		-120	5.85	7.01	8.54
		-60	2.17	4.41	5.12
α -D- 4 C ₁	-60 (C2-OH axial)	0	4.11	5.29	5.15
		60	0.21	1.85	1.61
		120	2.50	4.02	4.20
		180	3.44	4.85	5.00
		-120	4.58	6.11	6.03
		-60	3.81	5.00	5.07
β -D- 4 C ₁		0	4.31	5.05	3.10
		60	2.59	3.37	6.40
		120	5.89	8.25	10.88
		180	8.28	10.48	8.28
		-120	7.64	9.57	6.45
		-60	4.01	5.66	2.63

Table 4. The calculated anomeric energies in R1-O5-C1H(R3)-O1-R2 systems.

R1	R2	R3	Anomeric energy (kcal mol ⁻¹)	Exo-anomeric energy (kcal mol ⁻¹)		Reference
				α -D- ⁴ C ₁	β -D- ⁴ C ₁	
H	H	H	2.2 ^a (4.7) ^b [3.75] ^c	2.2 (4.7) [3.75]	4.4 (6.5) [5.09]	Vishveshwara and Rao (1982) Jeffrey <i>et al</i> (1972) Jeffrey <i>et al</i> (1978)
CH ₃	H	H	(3.0)	(4.3)	(6.4)	Jeffrey <i>et al</i> (1974)
CH ₃	CH ₃	H	(2.57)	(2.57)	(5.09)	Jeffrey <i>et al</i> (1978)
			1.57	1.57	1.76	Vishveshwara and Rao (1982)
H	H	CH ₃	2.49	3.08	5.01	Present work
CH ₃	H	CH ₃	(2.44)			Jeffrey and Yates (1981)
CH ₃	CH ₃	CH ₃	0.61	7.24	9.2	Present work
H	H	CH ₂ -OH axial	2.4 (4.49)	3.23	5.7	Present work Present work
CH ₃	H	CH ₂ -OH axial	(2.89)			Jeffrey and Yates (1981)
CH ₃	CH ₃	CH ₂ -OH axial	0.18	7.25	10.1	Present work
H	H	CH ₂ -OH equatorial	2.17 (3.89)	2.12	4.24	Present work Present work
CH ₃	H	CH ₂ -OH equatorial	(1.74)			Jeffrey and Yates (1981)
CH ₃	CH ₃	CH ₂ -OH equatorial	0.12	15.70	18.0	Present work

* The values represented without any bracket are obtained at the STO-3G level; ^b Numbers in parentheses are the 4-31G values; ^c Numbers in square brackets are the 6-31G* values.

energy value of ϕ_5 are given in table 4. As in the model systems for 2-deoxy sugars, the *exo*-anomeric energy is higher for β -D-⁴C₁ than for α -D-⁴C₁ configurations.

3.4 2,2-dimethoxyethanol

The computed energies as functions of ϕ_3 and ϕ_5 corresponding to the α -D-⁴C₁ and β -D-⁴C₁ configurations with the C2-OH equatorial and C2-OH axial orientations are given in table 5. The *exo*-anomeric energies were calculated in the same way as for 1,1,2-trihydroxyethane and are given in table 4. In some conformations ($\phi_3 = 0^\circ$ and -60° for α -D-⁴C₁) due to the closeness of the bulky methyl groups the energies are very high (table 5). The energy difference between that for β -D-⁴C₁ and α -D-⁴C₁ configurations with C2-OH equatorial is only 0.12 kcal mol⁻¹ (considering the lowest energy conformation with respect to ϕ_5), indicating that the anomeric energy is very small in systems with methoxyl substituent. Similarly the energy difference between that for β -D-⁴C₁ and α -D-⁴C₁ configurations with C2-OH axial is (0.56-0.38) = 0.18 kcal mol⁻¹.

Table 5. STO-3G conformational energies of 2,2-dimethoxyethanol.

Configuration ^a	ϕ_4	ϕ_3	ϕ_5		
			60	180	-60
α -D- ⁴ C ₁	180	0	219.80	219.70	217.80
	(C2-OH equatorial)	60	2.23	1.84	0.00 ^b
		120	4.68	3.38	2.75
		180	18.04	15.71	99.16
		-120	30.18	29.71	120.20
		-60	225.90	—	—
β -D- ⁴ C ₁		0	5.78	8.24	8.61
		60	7.63	8.91	9.01
		120	120.34	30.51	31.25
		180	101.13	18.16	20.78
		-120	4.48	5.54	7.14
		-60	0.12	2.40	3.06
α -D- ⁴ C ₁	-60 (C2-OH axial)	0	218.15	219.13	219.04
		60	0.38	1.64	1.38
		120	2.80	4.00	4.11
		180	7.63	8.91	9.00
		-120	22.90	24.30	23.95
		-60	224.98	225.90	225.80
β -D- ⁴ C ₁		0	7.87	8.06	6.36
		60	17.63	16.86	98.85
		120	30.02	31.31	120.59
		180	10.69	12.53	10.68
		-120	6.28	7.75	4.82
		-60	2.22	3.43	0.56

(Angles in degrees and energies in kcal mol⁻¹)^a as in table 1; ^b total energy = -376.9500425 hartrees.

lowered from those obtained using standard bond angles. The anomeric energy with C2-OH equatorial is equal to 0.37 kcal mol⁻¹ and with C2-OH axial it is (0.88 - 0.43) = 0.45 kcal mol⁻¹.

4. Discussion

From the simplest model of methanediol a closer model of pyranosides is approached by substituting the hydrogens on O5, and O1 by methyl groups and the hydrogen on C1 by methyl and hydroxymethyl groups as the case may be. Since the theoretical studies carried out here do not take into account the solvent effect or the intermolecular interactions, the results presented refer to isolated molecules in vacuum. The results presented above and those of previous theoretical studies summarised in table 4 bring out the following points.

(1) As the model system is closer to pyranosides, the theoretically computed anomeric energy decreases and the *exo*-anomeric energy of the α and β forms increases.

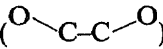
Table 6. STO-3G conformational energies of 2,2-dimethoxyethanol using optimized angles given in Gorenstein *et al* (1977).

Configuration ^a	ϕ_4	ϕ_3 (degrees)	ϕ_5	Total energy (hartrees)	Relative energy (kcal mol ⁻¹)
α -D- ⁴ C ₁	180	60	-60	-376.9521362	0.00
β -D- ⁴ C ₁	180	-60	60	-376.9515434	0.37
α -D- ⁴ C ₁	-60	60	60	-376.9514508	0.43
β -D- ⁴ C ₁	-60	-60	-60	-376.9507408	0.88

^a as in table 1.

C1 get methylated. Thus, as the model system becomes closer to the pyranoside, the theoretically computed anomeric energy decreases. Similar trends are predicted both by the STO-3G and the 4-31G basis sets, although the STO-3G anomeric energies are smaller compared to the 4-31G values. The experimentally reported anomeric energies range from 0.55 to 2.2 kcal mol⁻¹ (Durette and Harton 1971; Stoddard 1971). The various entries in the table lead us to conclude that the anomeric energy of 4.7 kcal mol⁻¹ obtained for methanediol by the *ab initio* method for the first time (Jeffrey *et al* 1972) at the 4-31G level can in fact approach the experimental value with the improved model and the increased level of sophistication in the basis set. The theoretical estimates of the *exo*-anomeric energies increase on methylation of C1 and oxygens (which can be clearly attributed to steric effect), for which although experimentally computed values are not available all the observed crystal structures of α and β methyl pyranosides (Jeffrey *et al* 1978; Jeffrey and Taylor 1980) correspond to (*g*, *g*) and (*t*, *g*) conformations respectively.

One point that emerges out of the results tabulated in table 4 is that the order of anomeric energy as a function of substituent on C1 as given by Allinger (1984) i.e., methoxy > hydroxy does not correspond to the theoretical estimate. Perhaps in this case as mentioned in §1, the experimental estimate of anomeric energy includes the interaction of the aglycone with other atoms of the pyranosides and the interaction with the solvent molecules.

(2) The results of the model compounds containing the C2-OH group show that the anomeric energy is greater when the group is axially oriented than when it is in the equatorial position. This has been recognised as the Δ^2 -effect (Reeves 1949; Durette and Harton 1971) which can be understood in terms of the dipolar interactions. The C-O bonds on adjacent carbon atoms () interact more favourably in the *trans* orientation than in the *gauche* orientation. This phenomenon is different from the *gauche* effect (Wolfe 1972), in which the preference for the *trans* and the *gauche* orientations of the polar bonds is reversed. This happens because the bonds interacting in the systems exhibiting the *gauche* effect have opposite polarity. The difference between the two types of interactions are depicted in figure 5, where 5a, 5b and 5c correspond to the models of β -⁴C₁ pyranose, α -⁴C₁ pyranose and a model for the *gauche* effect respectively. The arrows in the figure indicate the direction of the dipoles and it can be seen that the *gauche* interactions in figure 5a are unfavourable and that in 5c are favourable when the C2-OH is axially oriented as in the β -⁴C₁ pyranose and that

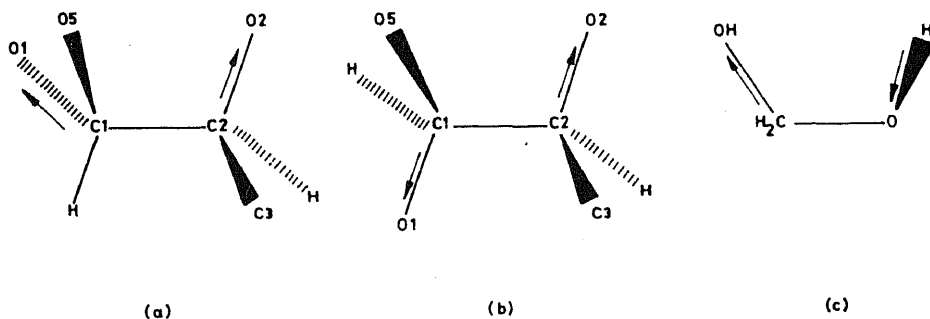


Figure 5. The dipolar interactions in models representing (a) β -C2-OH axial, (b) α -C2-OH axial and (c) *gauche* effect.

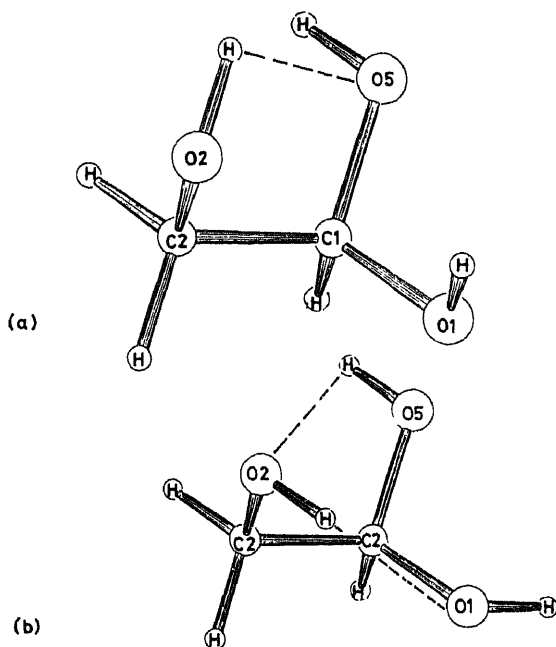


Figure 6. Ortep projections of 1,1,2-trihydroxyethane (a) $(\phi_4, \phi_5) = (60^\circ, 60^\circ)$ and (b) $(\phi_4, \phi_5) = (-60^\circ, -60^\circ)$.

the C2–O2 bond dipole has *gauche* interaction with both the C–O bonds of the O–C–O fragment (figure 5a). The C2–O2 bond makes a *gauche* and a *trans* interaction with the two dipoles of the O–C–O fragment in the axially oriented α - 4C_1 (figure 5b), equatorially oriented β - 4C_1 and α - 4C_1 pyranoses. Thus, the β -form of the axially oriented C2–OH is more destabilized than the equatorial orientation, leading to the Δ^2 -effect.

The magnitude of this dipolar interaction leading to the Δ^2 effect however depends on factors like the substituents on other atoms of the ring, the solvent and so on. For

instance, the above studies on the isolated model systems show that the tendency to form a good hydrogen bond is favoured as far as possible. In all the models with a C2-OH group, when one considers the conformations with the O2 being approximately equidistant from O1 and O5, the O2-H bond prefers to orient towards O1 and O5. This is perhaps due to the fact that the lone pairs of O1 are oriented towards O2, whereas the lone pairs of O5 point away from O2, thus resulting in a better hydrogen bond in the cases where O2-H is oriented towards O1. Thus the destabilization due to the axial disposition of C2-OH is further modified by interactions of the hydrogen bond type. In the model 1,1,2-trihydroxyethane with C2-OH axial, the β - 4C_1 form is stabilized by two H-bond-like interactions as shown in figure 6. Since O5 has a CH₃ group in 1-methoxyethanediol, the O5-H...O2 interaction is absent resulting in the reduced stability of the β - 4C_1 form in this model compound. This is in agreement with the 4-31G estimated values for the Δ^2 effect (including H-bond type of interactions) in 1,1,2-trihydroxyethane (0.6 kcal mol⁻¹, table 4) and 1-methoxyethanediol (1.2 kcal mol⁻¹, Jeffrey and Yates 1981). The STO-3G evaluated Δ^2 effects are generally very low (table 4) probably because it underestimates the dipolar interactions.

Thus, the above detailed analysis confirms the qualitative description of the Δ^2 -effect given by Reeves (1950) which states that the destabilization of the β -form arises due to the unfavourable dipolar interaction when the C2-OH is axially oriented. The magnitude of this effect is however dependent to a considerable extent on other intra and intermolecular interactions.

5. Conclusions

When the anomeric effect is defined as the property directly associated with the -O5-C1-O1- fragment of carbohydrates, the study of a series of model compounds have led to the following conclusions:

- (1) In all the model compounds studied, the anomeric effect decreases when O1 has a -CH₃ substituent in place of hydrogen. Hence, the experimentally observed reverse trend must be due to interactions not directly connected with the O-C-O fragment.
- (2) The Δ^2 effect, as suggested by Reeves is due to dipolar interactions and it is different from the *gauche* effect. The actual magnitude of this effect depends on other types of interactions which occur in a given system.

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Photoprocesses in sodium decyl sulphate micellar media

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Abstract. The absorption and fluorescence behaviour of thionine dye in sodium decyl sulphate (SDS) medium has been studied in detail. The transient spectra and kinetics of decay of semithionine species produced by photoreduction of thionine by ferrous ions has been studied using flash photolysis technique. The results have been compared with those in neat aqueous medium and in sodium lauryl sulphate (SLS) media published earlier. It was found that the decay of semithionine which is kinetically second order in neat aqueous medium becomes pseudo first order as in the SLS medium; however unlike in the latter case, the pseudo first order rate decreases with increasing surfactant concentration at all concentrations of ferric ion. The effect of electrolyte concentration on transient semithionine spectra and decay kinetics has also been studied. It was found that with increasing NaCl concentration the transient absorbance decreases and the decay slowly reverts back to second order as in aqueous medium. In SDS medium as compared to SLS a much higher concentration of NaCl is needed for the reaction to become second order which is attributed to stronger binding of ferric ions to the SDS micelles.

Keywords. Photoprocesses; sodium decyl sulphate medium; thionine dye; dye-surfactant charge pair complex.

Introduction

The behaviour of dyes in organised assemblies such as micelles of surfactant molecules is important for understanding the thermal and light induced reactions in biomembranes (Singhal *et al* 1970; Hevesi *et al* 1970). The relevance of these studies to light energy conversion has also been recognised (Kiwi *et al* 1982). In this connection the thionine (TH⁺)-ferrous system is of considerable interest (Rabinowich 1940; Clark and Bert 1975; Suda *et al* 1978; Kamat *et al* 1977, 1978). Reactions of photo-excited and radical species occurring in this system show distinctly different behaviour in sodium lauryl sulphate (SLS) micellar medium as compared to that in a neat aqueous solution (Guha *et al* 1979, 1982 and 1985). There are changes in the absorption spectrum and decrease in fluorescence intensity at SLS concentrations below the critical micelle concentration (CMC). These changes have been attributed to the formation of a dye-surfactant charge pair complex (Guha *et al* 1982). At SLS concentrations above the CMC this charge pair complex breaks and the dye gets solubilized in the micellar Stern layer. The decay of semithionine radical (TH₂[•]) formed by photoreduction, which is kinetically second order process in neat aqueous solutions, then becomes pseudo first order in the micellar medium. This has been attributed to the reoxidation of semithionine by ferric ions adsorbed on the same micelle surface (Guha *et al* 1985). In order to determine whether the different behaviour in the micellar system is dependent on the surfactant forming the micelle, detailed studies were undertaken in a sodium decyl sulphate (SDS) medium, the results of which are reported in this paper.

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2. Experimental

Thionine (Fluka, puriss grade) was purified as described earlier (Guha *et al* 1982). SDS was purified by repeated extraction of its aqueous solution with distilled diethyl ether, followed by evaporation and vacuum drying at slightly elevated temperature (50–60 °C). Ferrous solutions prepared from $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (non 'AnalaR' grade) contained ferric ion as an impurity and this impurity level was $\approx 1.36 \times 10^{-5} \text{ mol dm}^{-3}$ in a $0.015 \text{ mol dm}^{-3}$ ferrous solution. In those experiments where the solutions contained more than this minimal ferric ion concentration the latter was adjusted by addition of calculated amounts of Fe^{3+} in the form of 'AnalaR' (non) ferric alum. For some experiments ferric free solutions were also used which were prepared by dissolving freshly polished, cleaned E. Merck 68 iron wire in deaerated $2 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$. All other chemicals were the purest commercially available and were used as such. Stock solutions of SDS, thionine, ferrous and ferric (concentrations as required) were separately prepared in $8.9 \times 10^{-4} \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ (pH 1.75). Required aliquots of these were mixed together (surfactant solution added last) and diluted to give a bulk pH of 2.5–2.7. Triple-distilled water was used for preparation of solutions and dilutions. Absorption spectra were recorded on a Hitachi Model 330 spectrophotometer and fluorescence measurements were carried out using an Aminco-Bowman (Model 4-8202B) spectrofluorometer. The flash-photolysis apparatus and the method of deoxygenation of the solutions have been described earlier (Guha *et al* 1985). The decay of semithionine was monitored by following its absorbance near λ_{max} of 780 nm.

3. Results and discussion

3.1 Absorption and fluorescence behaviour

The results of both absorbance and fluorescence intensity measurements for $10^{-5} \text{ mol dm}^{-3}$ thionine at different SDS concentrations are given in figure 1. The general pattern of spectral changes with surfactant concentrations is as reported earlier in the case of SDS (Guha *et al* 1982). Thus from figure 1 it can be seen that the disappearance of the thionine absorption band at 598 nm is accompanied by the appearance of new bands at 515 nm and 635 nm. At surfactant concentrations beyond cmc these bands at 515 nm and 635 nm disappear and the band at 598 nm reappears with enhanced extinction coefficient. The cmc value for SDS derived from the plot of absorbance at 598 nm (λ_{max} of TH^+ in aqueous solution at pH ≈ 2.5) versus SDS concentration is $\approx 3.0 \times 10^{-2} \text{ mol dm}^{-3}$. No significant variation of the cmc value was observed in HCl, H_2SO_4 and neutral media. Considering the fact that the use of a dye probe gives a somewhat lower value for cmc (Mukherjee and Mysels 1955) this cmc value is in good agreement with the reported value of $3.2 \times 10^{-2} \text{ mol dm}^{-3}$ for SDS (Fendler and Fendler 1975). For the SDS system the extent of formation of dye-surfactant complex is maximal at surfactant concentration of $8.9 \times 10^{-4} \text{ mol dm}^{-3}$, as

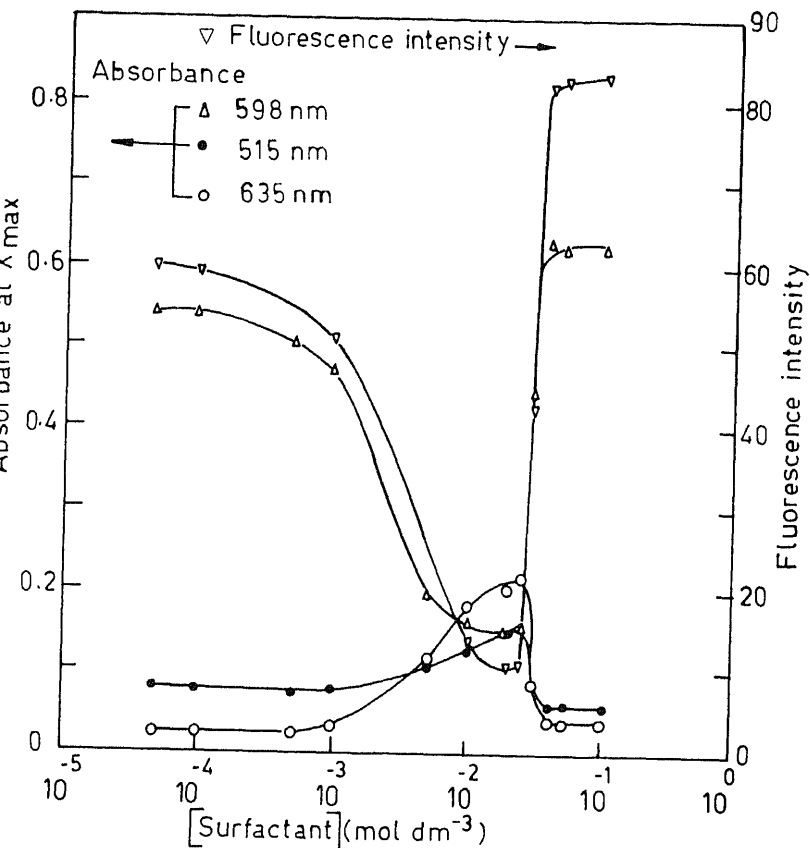


Figure 1. Effect of SDS concentration on thionine absorbance and fluorescence ($\text{TH}^+ = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} \sim 2.7$).

mer anions $[\text{SO}_4^--(\text{CH}_2)_9-\text{CH}_3]$ and hence greater probability of forming a π complex such as is shown in chart 1. On the other hand in the micellar medium

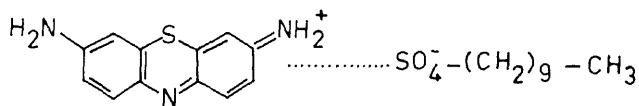


Chart 1.

less chance of formation of such a complex as the more hydrophobic part of the molecule tries to penetrate into the hydrophobic core of the micelle, the highly charged amino group being held by the electrostatic field of the negatively charged headgroups of the surfactant molecules. A similar situation exists in the

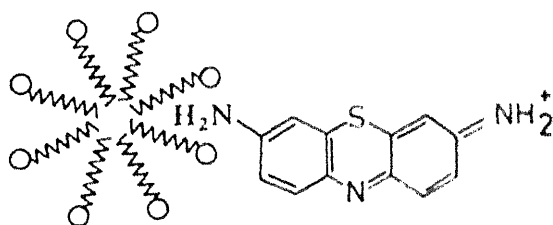


Chart 2.

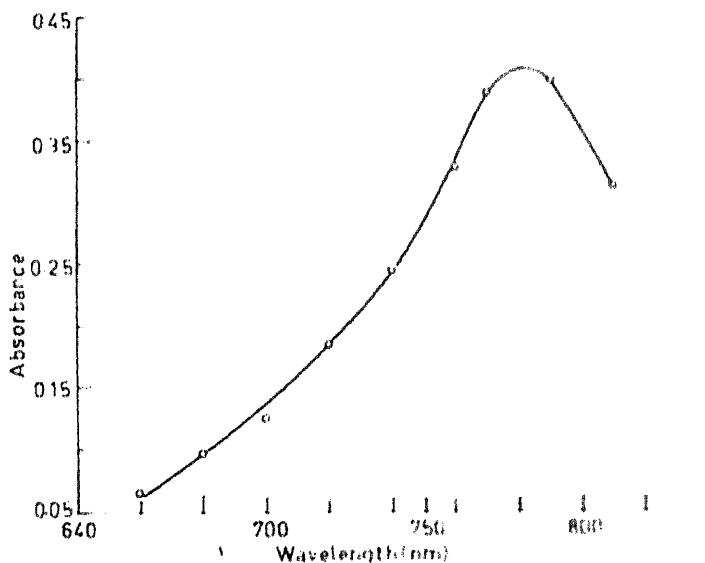


Figure 2. Transient spectrum of semithionine in SDS micellar medium at pH = 2⁺ (concentrations in mol dm⁻³: TH⁺ = 5×10^{-6} , SDS = 0.05, Fe²⁺ = 0.015, Fe³⁺ = minimal).

complex band disappears and the dye band reappears. The increased absorption and fluorescence in the micellar region may be attributed to the fact that the dye in the micellar environment has a different extinction coefficient and radiative life-time as compared to the pure aqueous environment (Guha *et al* 1985). From a correlation of the change in extinction coefficient of thionine with the medium polarity, the dielectric constant of the SDS micellar environment around thionine was evaluated to be 57. This is comparable with the value of 56 estimated earlier in the case of SDS (Guha *et al* 1982).

3.2 Transient spectra in SDS medium

The basic photoprocesses occurring in the thionine ferrous system are well known (Hatchard and Parker 1961; Ferreira and Harriman 1977). The transient semithionine spectrum observed in a micellar solution of SDS (surfactant concentration = 0.05 mol dm⁻³) is given in figure 2. At higher surfactant concentrations there is no qualitative change in the nature of the spectrum. As in the case of SDS micellar media

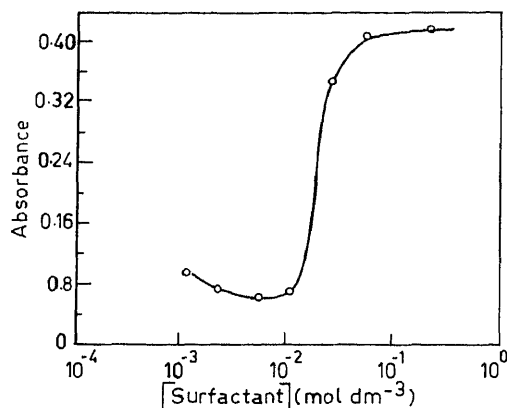


Figure 3. Effect of SDS concentration on the absorbance of semithionine at 785 nm (pH $\sim$ 2.7; concentrations in mol dm⁻³: TH⁺ = 5×10^{-6} ; Fe²⁺ = 0.015; Fe³⁺ = minimal).

(Guha *et al* 1985) there is a shift in the $\lambda_{\max}$ of about 25 nm compared to the spectrum in the neat aqueous medium and also no evidence of the fine structure. Thus semithionine ferrous interaction is suppressed in the SDS micellar medium also. The plot of semithionine absorbance versus surfactant concentration is given in figure 3. It can be seen that with increasing surfactant concentration the transient absorbance first decreases to a minimum at about $8-9 \times 10^{-3}$ mol dm⁻³ and thereafter increases sharply. This compares very well with changes in the absorbance of ground state thionine. Thus it seems that only uncomplexed thionine is involved in the photo-reduction by Fe²⁺ to form the semithionine species.

3.3 Decay kinetics

As reported earlier (Guha *et al* 1979) in homogeneous aqueous solutions semithionine decays by a second order process, attributed to its dismutation, with a rate constant of 2.4×10^9 dm³ mol⁻¹ sec⁻¹. In SDS solutions the behaviour is found to be different. At SDS concentrations near the CMC, the decay deviates from pure second order, and could be resolved into a first order and a second order component.

At surfactant concentrations above the CMC, the decay was found to be slower and purely first order. However, unlike in the case of SLS (Guha *et al* 1985) the first order rate constant (k_1) was found to decrease with increasing concentration of surfactant. The experiments carried out under ferric-free conditions prepared by the dissolution of AnalaR iron wire in deaerated H₂SO₄ and at higher concentration of ferric ion (1×10^{-4} mol dm⁻³) show similar behaviour as in minimal ferric solutions. The results of these are shown in figure 4. To see whether the decrease is due to increase in viscosity with increasing surfactant concentration, viscosity measurements were made. For a diffusion controlled reaction, the rate constant is directly proportional to the sum of the diffusion coefficients of reacting species, while the diffusion coefficients are inversely proportional to the viscosity of the medium. Hence the rate constant should be inversely proportional to viscosity (η) or $k_1\eta$ should be constant. As can be seen from the data given in table 1, the rate constant variation does not conform to the behaviour expected for a diffusion controlled reaction.

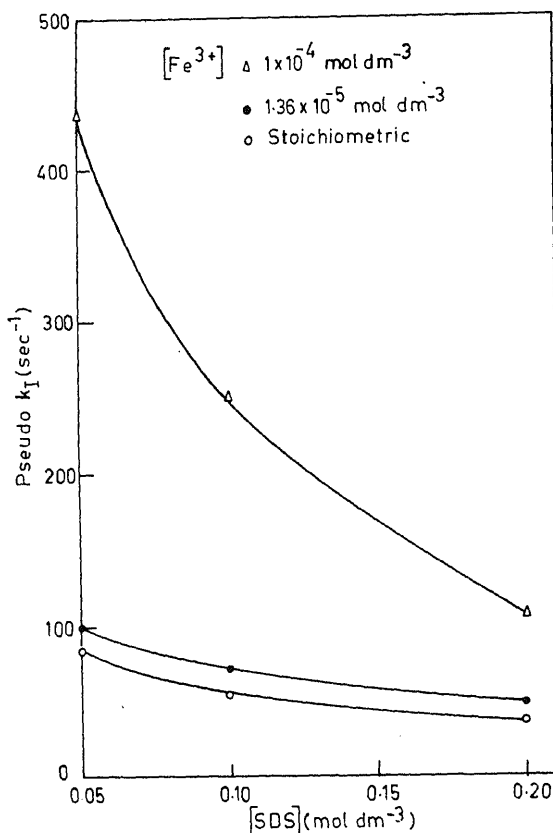


Figure 4. Effect of SDS concentration on pseudo first order rate at different Fe^{3+} concentrations (pH ~ 2.7 ; concentrations in mol dm^{-3} ; $\text{TH}^+ = 5 \times 10^{-6}$; $\text{Fe}^{2+} = 0.015$).

Table 1. Effect of SDS concentration on the viscosity of the medium and the rate constant for semithionine decay. (Minimal $[\text{Fe}^{3+}]$).

[SDS] (mol dm^{-3})	Observed rate constant k_I (sec^{-1})	Viscosity η (cp)	$k_I \cdot \eta$
0.05	0.983×10^2	0.91	0.90×10^2
0.1	0.700×10^2	0.95	0.66×10^2
0.2	0.495×10^2	1.04	0.51×10^2

At a fixed concentration of surfactant (0.05 mol dm^{-3}) the first order rate constant was found to increase with increasing concentration of added Fe^{3+} ions as observed in the case of SLS earlier. The plot of $\log k_I$ vs $\log [\text{Fe}^{3+}]$ was found to be linear (figure 5) indicating that k_I is proportional to Fe^{3+} ion concentration. Hence the reaction with which semithionine disappears seems to be pseudo first order with respect to Fe^{3+} in the SDS micellar medium also and is inferred to be the reoxidation of semithionine by

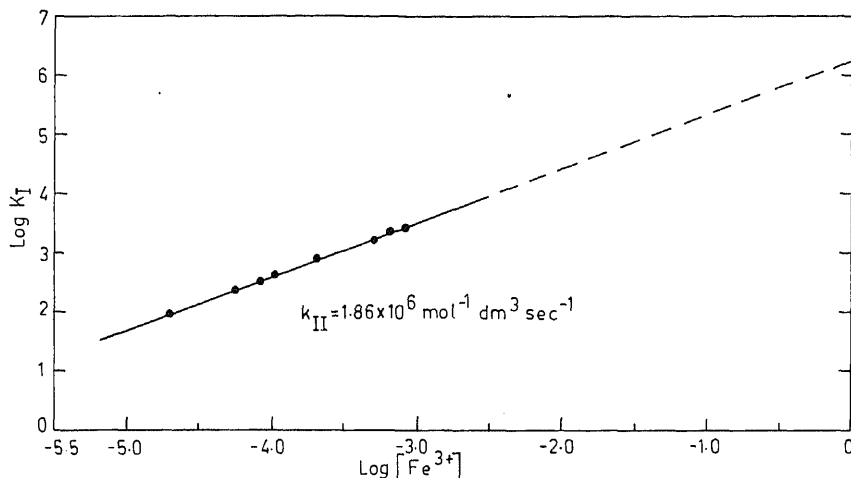


Figure 5. Dependence of first order decay rate of semithionine in SDS micellar solution on Fe^{3+} concentration (pH ~ 2.7 ; concentrations in mol dm^{-3} : SDS = 0.05, Fe^{2+} = 0.015, $\text{TH}^+ = 5 \times 10^{-6}$).

ferric ions:



In the case of SLS micellar medium this has been confirmed by observing the recovery of the photobleaching of thionine with the same rate constant as for the decay of semithionine (Guha *et al* 1985). The intercept of the linear plot in figure 5 gives a value of $k_{II} = 1.86 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for the rate constant of this reoxidation reaction as compared to a value of $6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ deduced in the case of the SLS micellar medium (Guha *et al* 1985). It may be noted that these rate constants are not true bimolecular rate constants as applicable to a homogeneous medium, but must be interpreted as representing the probability of occurrence of reaction between species adsorbed or solubilized in the micelle. The value for this rate constant in a homogeneous aqueous solution is an order of magnitude higher: $7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ (Ferreira and Harriman 1977). Although the values are of the same order of magnitude in the SLS and SDS micellar media it is appreciably smaller in the latter. This would imply that the semithionine and Fe^{3+} are more tightly bound in the SDS micelle as compared to the SLS one. The same conclusion is reached from a study of the effect of electrolytes (see §3.4).

Findings considerably at variance with ours have been reported in a recent paper (Mackay and Grätzel 1985). These are: the reoxidation reaction is not enhanced in the SLS micellar medium and the semithionine decay as monitored at 404 nm is second order. In the light of this report we performed a set of experiments exactly under the conditions given in their paper with respect to pH and the concentrations of thionine, ferrous and ferric, as well as the monitoring wavelength. Even under these conditions we obtained the same result as reported here and in the previous publication (Guha *et al* 1985). In this connection we wish to add that the results of experiments in micellar

Table 2. Electrolyte effect on semithionine absorbance in SDS micellar media.

[NaCl] (mol dm ⁻³)	Absorbance at 770 nm
0	0.42
1.0	0.44
1.5	0.35
1.8	0.31
2.0	0.25
2.5	0.22

method of preparing the reaction mixture. These have been meticulously controlled in our work as detailed in the experimental section.

3.4 Effect of electrolytes

In the presence of NaCl, the transient semithionine spectrum in SDS micellar medium did not exhibit any change in $\lambda_{\max}$ though there was a decrease in absorbance with increasing NaCl concentration (table 2). This can be explained as due to the effect of electrolytes on the structure of the ionic micelles and the phenomenon of ion exchange occurring on the micellar Stern layer (Ikeda *et al* 1981; Quina and Chaimovich 1979; Cuccovia and Chaimovich 1982; Kishore and Moorthy 1983). Thus on addition of high concentrations of NaCl we expect the adsorbed Fe^{2+} ions to be displaced from the Stern layer by the cations of the added electrolyte. Consequently the concentration of Fe^{2+} ions available for photoreduction of excited thionine decreases, leading to a decreased extent of photoreduction, and hence, the decrease in the absorbance of semithionine with increasing NaCl concentration.

A second effect of the addition of NaCl to the SDS micellar system is that the decay of the semithionine reverts back to second order. As inferred in the case of SLS, this is due to the displacement of Fe^{3+} ions from the micelle surface by Na^+ ions as a result of which the reoxidation of semithionine by Fe^{3+} ions is not possible any more and the dismutation of semithionine becomes dominant. However, in the SDS case, as compared to SLS, we need much higher concentrations of electrolyte for the reaction to become second order. This would point to a tighter binding of Fe^{3+} ions in the former case. It is also observed that the second order slope ($k_{\text{II}}/\epsilon \cdot 1$) increases with NaCl concentration. This variation is given in table 3. In the system there are two possible effects which can be expected to cause variation in the reaction rate. As the ionic strength of solution increases with increasing NaCl concentration the rate of the reaction between two like-charged species is expected to increase, but at the same time with increasing NaCl concentration there is also observed an increase in the viscosity of solution which brings down the rate of diffusion controlled reactions. The fact that the observed rate constant increases with increasing NaCl concentration seems to indicate that the effect of ionic strength dominates over that of viscosity. A more detailed account of these effects is

Table 3. Variation of 2nd order slope for semithionine decay with NaCl concentration in SDS micellar media.

[NaCl] (mol dm ⁻³)	Second order slope $\times 10^{-3}$ (sec ⁻¹)
1.0	1.56
1.5	3.13
1.8	6.20
2.0	9.02
2.5	12.1

3.5 Pseudophase model of kinetics in micellar media

The micellar effects on the kinetics of reactions have been recently explained on the basis of the pseudophase model (Bunton *et al* 1977; Bunton 1979). The applicability of this model to the reactions of semithionine has been discussed previously in the case of SLS medium (Guha *et al* 1985). In the SDS micellar system, as in the case of SLS, the reoxidation of semithionine by Fe^{3+} is an order of magnitude slower than in the neat aqueous medium. Therefore on the basis of the pseudophase model, there is expected to be a monotonous decrease in the rate of this reaction with increase in SDS concentration due to the pseudophase dilution effect. This was hardly noticeable in the case of SLS with no externally added Fe^{3+} , but is definitely seen in the SDS system (figure 4). However, in both cases the effect is quite marked in presence of added Fe^{3+} ions. Similarly, in presence of added NaCl when the dismutation of semithionine dominates over its reoxidation by Fe^{3+} , the pseudophase dilution effect is again clearly discernible.

Acknowledgements

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What is the maximum yield in the solid state cinnamic acid dimerisation? A combinatorial mathematical approach

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Abstract. Recurrence relations have been employed to obtain the maximum possible theoretical conversion in a topochemically controlled organic solid state reaction. Experimental deviations from this analytical value of $\approx 82\%$ reflect the importance of defects, molecular relaxation and surface phenomena in real crystals.

Keywords. Configuration; recurrence relation; power series; partial fractions; topochemistry; cinnamic acid; photodimerisation; maximum yield.

1. Introduction

One of the oldest and best studied of organic solid state reactions is the photodimerisation of *trans*-cinnamic acid in uv light (Schmidt *et al* 1964). This is a good example of topochemical control in organic crystals because the three-dimensional structure of the starting material exclusively determines the chemical structure of the product.

In the α -form, the nearest neighbours are related by a centre of symmetry and react to give an inversion symmetry truxillic dimer. In the β -form, however, the nearest neighbours are translationally related and the product is a mirror-symmetry truxinic dimer. The crystal symmetry of the monomer is thus preserved in the molecular symmetry of the dimer.

One of the interesting and less-studied aspects of this reaction is the fact that the α - and the β -forms of the reactant differ in the maximum possible theoretical conversion to dimer (Schmidt *et al* 1964). In the α -form each molecule has only one nearest neighbour. This neighbour is related to it by a crystallographic centre of symmetry and photoreaction is only possible between two such neighbours. Thus close to quantitative conversions are possible and are in fact realised in practice (95–100%, figure 1). However, in the β -form all the molecules are related by translation in a row to form the stack. Each molecule in the stack can react with either of its two equally close nearest neighbours. Therefore, as a result of independent events in the stack, a monomer molecule may find itself eventually isolated (figure 2). Therefore, if the product does not recrystallise as a separate phase, yields of photodimer can never be quantitative. In fact, maximum yields of dimer can be as low as 30% for the β -acids (Schmidt *et al* 1964).

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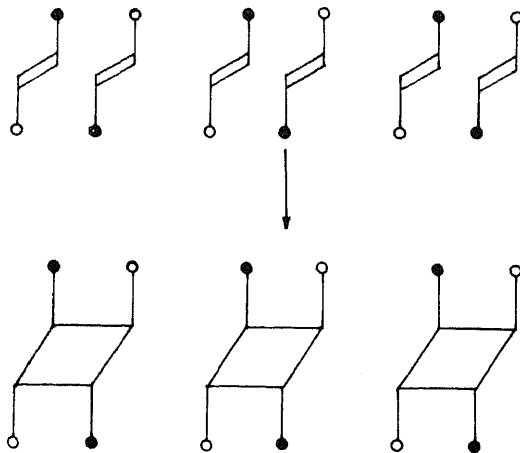


Figure 1. Photoreaction of crystalline α -cinnamic acid (schematic).

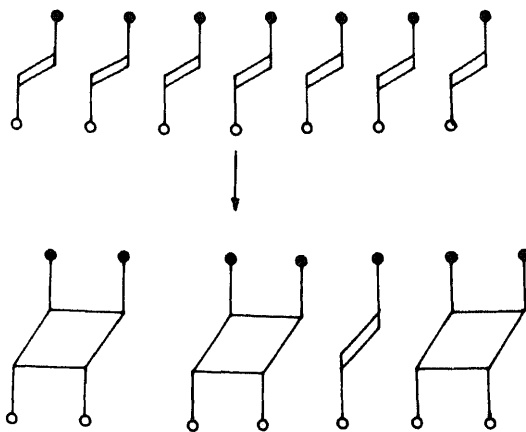


Figure 2. Photoreaction of crystalline β -cinnamic acid (schematic).

Can one, in fact, determine what the maximum possible theoretical yield is in a photoreaction of the β -crystals? The answer is yes, if a few simplifying assumptions are made. The result can be obtained analytically using recurrence relations.

2.1 Chemical formulation of the problem

The basic assumptions for the theoretical analysis of the photoreaction are as follows:

- (a) Reaction is possible everywhere in the crystal at the outset and anywhere in the unreacted portions during the course of the reaction.
- (b) Reaction at any molecule is with one of its two translationally related neighbours in the stack. If one neighbour has already reacted, reaction is only possible with the other. If both neighbours have reacted, the molecule cannot react.
- (c) The reaction of molecules in one stack will not affect the molecules in any other

stack in the crystal. Within a stack, the probability that a reaction will occur at a particular site is not affected by a reaction having occurred nearby. In other words, each reaction is an independent event.

(d) The 'isolated' monomer molecules cannot crystallise out of the dimer matrix in the later stages of the reaction. This is a good assumption because quantitative yields are never obtained in the β -crystal photoreaction. In other words, the isolated monomers do not conglomerate and recrystallise during the later stages of the reaction as this would eventually lead to a quantitative yield of photo-product.

2.2 Mathematical formulation of the problem

The molecules can be abstractly represented by points in a line. A stack is such an arrangement of points. When two molecules react with each other, the corresponding points are joined to one another. Points that are not joined to any other point are called isolated points. The other points are called non-isolated points. Our chemical assumptions therefore mean that:

- (a) no two consecutive points can be isolated;
- (b) no point is joined to any point other than its predecessor or successor.
- (c) no point can be joined to more than one point. So, if p is joined to its successor q , then neither can p be joined to its predecessor, nor can q be joined to its successor.

Under these assumptions, we ask 'what is the probability that a point remains isolated?'

2.3 Theoretical analysis

We proceed as follows: first consider a finite sequence of n points and consider all possible configurations of these, called n -configurations, satisfying the above three requirements. Count the total number of isolated points in each of these configurations and compute the average number of isolated points in the n -configurations. Divide this number by n and take the limit as n tends to ∞ . The answer gives the probability of the occurrence of isolated points in an infinite sequence.

2.3a *Some notations:* For each positive integer n , we let

G_n = the number of n -configurations

and

g_n = the total number of isolated points in all these n -configurations put together.

Then the precise problem on hand is to compute $\lim_{n \rightarrow \infty} (1/n) \cdot (g_n/G_n)$ if it exists.

2.3b *Values of G_n and g_n :* For small values of n , the values of G_n and g_n can be directly computed. We list these values for our later use:

$$\left. \begin{array}{ll} G_1 = 1 & g_1 = 1 \\ G_2 = 1 & g_2 = 0 \\ G_3 = 2 & g_3 = 2 \end{array} \right\}$$

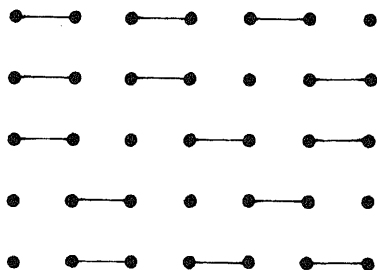


Figure 3. Five 7-configurations arranged in columns.

By way of explanation, we describe the details in one particular case, namely when $n = 7$. Figure 3 shows all possible 7-configurations.

Each column in figure 3 is a 7-configuration and there are five such. Thus $G_7 = 5$. If we count the total number of isolated points in all these, it is 7. Thus $g_7 = 7$.

2.3c A recurrence relation for G_n : Consider the sequence of numbers $G_1, G_2, \dots, G_n, \dots$. If a formula for the n th term G_n in terms of the previous terms, holds for all values of n , it is called a recurrence relation satisfied by this sequence. Presently we obtain one such relation. Let us assume $n \geq 3$.

Among all n -configurations, there are two types. These are: (1) those that start with an isolated point, and (2) those that start with a non-isolated point.

If an n -configuration starts with an isolated point, the second and third points are necessarily joined to each other, and the remaining points form an arbitrary $(n-3)$ -configuration. Therefore there are exactly as many n -configurations of the first type as there are $(n-3)$ -configurations of both types. The latter number is G_{n-3} .

If an n -configuration starts with a nonisolated point, then the first two points are joined to each other and what remains is an arbitrary $(n-2)$ -configuration. Thus there are exactly as many n -configurations of the second type as there are $(n-2)$ -configurations of both types. This latter number is G_{n-2} .

Putting these together, we obtain the formula,

$$G_n = G_{n-2} + G_{n-3}, \text{ for all } n \geq 3. \quad (2)$$

2.3d A recurrence relation for g_n : If an n -configuration is of the first type, then it has one isolated point more than its corresponding $(n-3)$ -configuration. Such n -configurations contribute $g_{n-3} + G_{n-3}$ isolated points, because, as we have already seen, G_{n-3} is the number of n -configurations of the first type.

If an n -configuration is of the second type, then it has exactly as many isolated points as its corresponding $(n-2)$ -configuration. Therefore such n -configurations contribute g_{n-2} isolated points.

Taking these together, we obtain

$$g_n = g_{n-2} + g_{n-3} + G_{n-3}, \text{ for all } n \geq 3. \quad (3)$$

2.3e Further values of G_n and g_n : Using these recurrence relations (2) and (3), not only can we check the validity of some values listed in (1), but can also compute the same

Table 1.

n	G_n	g_n	g_n/nG_n
5	3	3	1/5
6	4	6	1/4
7	5	7	1/5
8	7	12	3/14
9	9	17	17/81
10	12	24	1/5
11	16	36	9/44
12	21	50	50/273
13	28	72	9/49
14	37	102	34/185

computed only recursively, we have tabulated these values below upto the required stage.

Our problem is to find the limit of the sequence that appears in the last column of table 1. It is heartening to observe that each term here lies between 1/4 and 1/6. It will be shown that, eventually it lies between 1/5 and 1/6.

2.3f *An inequality for G_n* : We use the recurrence relations (2) and (3) now to prove that

$$G_{n-1} \leq G_n \leq (3/2)G_{n-1} \quad (4)$$

for all $n \geq 4$. Suppose this is true for $n = m-1$, $n = m-2$ and $n = m-3$. Then this is true for $n = m$ also, because

$$\begin{aligned} G_m &= G_{m-2} + G_{m-3} \text{ by (2)} \\ &\geq G_{m-3} + G_{m-4} \text{ because (4) is true for } n = m-2 \text{ and } n = m-3 \\ &= G_{m-1} \text{ by (2),} \end{aligned}$$

and further,

$$\begin{aligned} G_m &= G_{m-2} + G_{m-3} \text{ by (2)} \\ &\leq (3/2)(G_{m-3} + G_{m-4}), \text{ for (4) is true for } n = m-2 \text{ and } n = m-3, \\ &= (3/2)G_{m-1} \text{ by (2).} \end{aligned}$$

A look at (1) and table 1 shows that (4) is true for $n = 4, 5, 6$. Therefore, by the principle of induction (4) is true for all $n \geq 4$.

2.3g *At most 1/5*: We claim that for large n , the value of $g_n/(nG_n)$ is necessarily $\leq 1/5$. Suppose for some n we have,

$$(g_{n-2})/((n-2)G_{n-2}) \leq 1/5,$$

and

$$(g_{n-3})/((n-3)G_{n-3}) \leq 1/5. \quad (5)$$

Then

and

$$5g_{n-3} \leq (n-3) G_{n-3}. \quad (5')$$

Now

$$\begin{aligned} 5g_n &= 5(g_{n-2} + g_{n-3} + G_{n-3}), \text{ by (3),} \\ &\leq (n-2) G_{n-2} + (n-3) G_{n-3} + 5G_{n-3}, \text{ by (5'),} \\ &= n(G_{n-2} + G_{n-3}) + 2G_{n-3} - 2G_{n-2} \\ &\leq n(G_{n-2} + G_{n-3}), \text{ because } G_{n-3} \leq G_{n-2} \text{ by (4),} \\ &= nG_n \text{ by (2),} \end{aligned}$$

and therefore,

$$g_n/(nG_n) \leq 1/5. \quad (6)$$

Thus (5) implies (6) if $n \geq 6$. We check from table 1 that (6) holds for $n = 12, 13$ and 14. It follows by an inductive argument that (6) holds for all $n \geq 12$.

2.3h *At least 1/6:* Similarly, if for some n we have

$$g_{n-2}/((n-2) G_{n-2}) \geq 1/6,$$

and

$$g_{n-3}/((n-3) G_{n-3}) \geq 1/6, \quad (7)$$

then

$$6g_{n-2} \geq (n-2) G_{n-2},$$

and

$$6g_{n-3} \geq (n-3) G_{n-3}. \quad (7')$$

and therefore

$$\begin{aligned} 6g_n &= 6(g_{n-2} + g_{n-3} + G_{n-3}), \text{ by (3),} \\ &\geq (n-2) G_{n-2} + (n-3) G_{n-3} + 6G_{n-3} \text{ by (7'),} \\ &= n(G_{n-2} + G_{n-3}) + 3G_{n-3} - 2G_{n-2} \\ &\geq n(G_{n-2} + G_{n-3}), \text{ because } 3G_{n-3} \geq 2G_{n-2} \text{ by (4),} \\ &= nG_n \text{ by (2),} \end{aligned}$$

and therefore,

$$g_n/(nG_n) \geq 1/6. \quad (8)$$

Observing that (8) holds for $n = 5, 6, 7$, we obtain from the above that (8) holds for all $n \geq 5$.

2.3i *Final result:* Thus for $n \geq 12$, we have

$$1/6 \leq g_n/(nG_n) \leq 1/5,$$

and therefore the required probability also lies between these two numbers. In fact, $1/5$ and $1/6$ are not sharp bounds for the above proof to work. One can prove that if for some n we have

$$\max(G_n/G_{n-1}, G_{n-1}/G_{n-2}, G_{n-2}/G_{n-3}) \leq (\alpha-3)/2$$

and

$$\min \{g_m/(mG_m): m = n-1, n-2, n-3\} \geq 1/\alpha$$

then

$$g_m/(mG_m) \geq 1/\alpha \text{ for all } m \geq n.$$

A dual result gives an upper bound for $g_m/(mG_m)$. An expanded tabulation upto $n = 19$, can now be used to prove that $43/243 \leq (g_n/(nG_n)) \leq 34/185$ for all $n \geq 19$. This means that the required probability lies between 17.69 and 18.38%. Thus, when rounded off to the nearest integer, the answer is 18%.

The probability of occurrence of non-isolated points therefore lies between 81.72% and 82.31%.

2.4 Proof that $Lt_{n \rightarrow \infty} (1/n)(g_n/G_n)$ exists and its value

The proof of the existence of the limit and its calculation involve heavier mathematics, which is outlined below.

Consider the power series

$$G(x) = 1 + G_1x + G_2x^2 + G_3x^3 + \dots + G_nx^n + \dots$$

Using the recurrence relation (2), one obtains

$$G(x)(1 - x^2 - x^3) = 1 + x,$$

$$G(x) = (1 + x)/(1 - x^2 - x^3).$$

Differentiating this power series term by term and then multiplying throughout by x , we get

$$G_1x + 2G_2x^2 + \dots + nG_nx^n + \dots = (x + 2x^2 + 4x^3 + 2x^4)/(1 - x^2 - x^3)^2.$$

In a similar way, one obtains from (3)

$$g(x) = g_1x + g_2x^2 + \dots + g_nx^n + \dots = x/(1 - x^2 - x^3)^2.$$

Let

$$1 - x^2 - x^3 = (1 - \alpha x)(1 - \beta x)(1 - \bar{\beta}x). \quad (9)$$

Then these two expressions can be resolved into partial fractions,

$$\left. \begin{aligned} x/(1 - x^2 - x^3)^2 &= A_1/(1 - \alpha x) + A_2/(1 - \alpha x)^2 + A_3/(1 - \beta x) + A_4/(1 - \beta x)^2 \\ &\quad + A_5/(1 - \bar{\beta}x) + A_6/(1 - \bar{\beta}x)^2, \\ (x + 2x^2 + 4x^3 + 2x^4)/(1 - x^2 - x^3)^2 &= B_1/(1 - \alpha x) + B_2/(1 - \alpha x)^2 \\ &\quad + B_3/(1 - \beta x) + B_4/(1 - \beta x)^2 \\ &\quad + B_5/(1 - \bar{\beta}x) + B_6/(1 - \bar{\beta}x)^2. \end{aligned} \right\} \quad (10)$$

Each term on the right can be expanded as a power series. The coefficient of x^n is given totally by

$$A_1 \alpha^n + A_2 (n+1) \alpha^n + A_3 \beta^n + A_4 (n+1) \beta^n + A_5 (\bar{\beta})^n + A_6 (n+1) (\bar{\beta})^n$$

in the first, and by a similar expression in the second. Therefore

$$g_n = \frac{A_1 \alpha^n + A_2 (n+1) \alpha^n + A_3 \beta^n + A_4 (n+1) \beta^n + A_5 (\bar{\beta})^n + A_6 (n+1) (\bar{\beta})^n}{A_1 \alpha^n + A_2 (n+1) \alpha^n + A_3 \beta^n + A_4 (n+1) \beta^n + A_5 (\bar{\beta})^n + A_6 (n+1) (\bar{\beta})^n}.$$

Now $1/\alpha$ is the unique real root of $1 - x^2 - x^3$. Since $3/4$ is the approximate real root, α is approximately $4/3$. By comparing the coefficients in (9), $\alpha\beta\bar{\beta} = 1$. Therefore $|\beta| < 1$. So $|\beta|^n/|\alpha|^n$ is very small if n is large. When we divide both the numerator and the denominator of the above expression for $g_n/(nG_n)$ by α^n , we find therefore that the limit required is equal to the limit of $[A_1 + A_2(n+1)]/[B_1 + B_2(n+1)]$ which is easily seen to be equal to A_2/B_2 .

We next note from (10) that

$$A_2 = \lim_{x \rightarrow 1/\alpha} (1 - \alpha x)^2 x / (1 - x^2 - x^3)^2 \text{ and}$$

$$B_2 = \lim_{x \rightarrow 1/\alpha} (1 - \alpha x)^2 (x + 2x^2 + 4x^3 + 2x^4) / (1 - x^2 - x^3)^2.$$

Therefore

$$\begin{aligned} A_2/B_2 &= \lim_{x \rightarrow 1/\alpha} x / (x + 2x^2 + 4x^3 + 2x^4) \\ &= \alpha^3 / (\alpha^3 + 2\alpha^2 + 4\alpha + 2), \text{ and because } \alpha^3 = \alpha + 1, \\ A_2/B_2 &= (\alpha + 1) / (2\alpha^2 + 5\alpha + 3) = (\alpha + 1) / (2\alpha + 3) (\alpha + 1) \\ &= 1 / (2\alpha + 3). \end{aligned}$$

Thus the actual value of the limit is $1/(2\alpha + 3)$ where $1/\alpha$ is the unique real root of $1 - x^2 - x^3$ (since α is approximately 1.33, this limit is approximately equal to 0.177, i.e. 17.7%).

3. Experimental deviations from the theoretical value

3.1 The role of thermal defects

Our results show that under the idealised conditions assumed by us, the maximum yield of β -truxinic dimer from solid state photoirradiated β -cinnamic acid is 82%. In practice, experimental yields vary from as low as 60% to as high as 90% for different β -acids.

Deviations from the idealised value occur because the assumptions in §2.1 need not strictly hold in all cases. While assumption (b) is self-evident in any non-defect controlled reaction such as the cinnamic acid dimerisation, assumptions (a), (c) and (d) may be contravened in several instances.

It has been observed that the crystallographic short axes for β -cinnamic acids vary between 3.85 and 4.15 Å. While any value in this range of translational distances is sufficient to permit initial photoreaction, any such reaction will be accompanied by a reduction in the distance between reacting molecules from ≈ 4.0 Å to ≈ 1.6 Å. This reduction must result in a concomitant relaxation of the neighbouring unreacted molecules so that the 'new' distance between incipient reactive molecules is now greater than the short axis. For crystals with short axes of 4.0 Å or less, such a relaxation probably does not affect photoreactivity. However, if the short axis is greater than 4.0 Å, molecular relaxation that follows initial reaction could place molecules beyond the photoreactive 'threshold' of 4.2 Å. Recently we have studied a case (Sarma and Desiraju 1984) where such a phenomenon, involving violation of assumption (a), probably occurs. We have observed that while 2,4-chlorocinnamic acid (β -structure, short axis

3.88 Å) has a maximum dimer yield of 90 %, 6-chloro-3,4-methylenedioxcinnamic acid (β -structure, short axis 4.10 Å) will react to the extent of 70 % dimer only.

Yields of dimer in β -crystals greater than 82 % could arise due to autocatalysis, preferred surface reactions or to monomer crystallisation in the later stages of the reaction, in other words, in cases where assumptions 3 and 4 are not valid. However, this is not a situation often encountered and even Schmidt's definitive work in this area (Schmidt *et al* 1964) reports only three β -acids out of 14 where the maximum yields are significantly greater than 82 %.

While it is generally true that maximum yields in α -cinnamic acid solid state photodimerisations are very high, deviations from the theoretical value of 100 % may reflect the presence of thermal defects in the crystal. Such defects have been invoked in a recent study on the kinetics of topochemical process (Hasegawa and Shiba 1982) where it has been commented that the rates of these reactions decrease above an optimal temperature (T_{opt}). For α -cinnamic acid, T_{opt} is 20°C and this means that the mismatch between potentially reactive double bonds owing to thermal fluctuations may inhibit solid state photoreactivity to some extent at temperatures above 20°C. Hasegawa and Shiba's study reports reaction rates as a function of temperature but an entirely analogous set of results would probably be obtained if one were to measure maximum dimer yields in an α -crystal as a function of temperature. While the number of thermal defects could be obtained analytically, a corroborative number may probably be obtained experimentally from the maximum yield measurements.

Hasegawa and Shiba (1982) state that T_{opt} is rather high for hydrogen bonded crystals. It is possible that defects are better trapped in such crystals with a reduced probability of the crystal relaxing to an incipient reactive geometry. In complementary results (which demonstrate the reduced importance of defects for non-polar crystals) it has been observed that for α -symmetry compounds such as 2-benzyl-5-benzylidenecyclopentanone or α -benzylidene- γ -butyrolactone, the conversion to dimer is quantitative (Jones *et al* 1980; Kearsley and Desiraju 1985). Interestingly, in the crystal of 3,4-dimethoxycinnamic acid, where only half the molecules are in a potentially reactive centrosymmetric (α) arrangement, the maximum dimer yield is 44 % (Desiraju *et al* 1984). That this number is less than 50 % is possibly because of the importance of thermal defects, and almost certainly means that dimer and monomer molecular phases do not separate with the progress of the reaction. This confirms the validity of assumption (d) in such reactions.

3.2 Mathematical modelling of defect reactions

The analytical treatment in §2.3 follows from assumptions concerning an equal probability of photoreaction throughout the crystal. While this is more-or-less true for defect-free regions in the bulk, the situation may be quite different in the crystal boundaries.

Let us now consider the situation where the points near the boundary of each stack behave differently from the points in the interior, as stated below: there is a number m such that m points in each of the two ends are sure to react, and cannot remain isolated.

Then for a given n , not all n -configurations are to be considered, but only those in

It is observed that an n -configuration is eligible in our new counting exactly when (i) none of the m points in the upper end and m points in the lower end remain isolated and (ii) the remaining $n-2m$ points form a configuration that is eligible according to the earlier sense. Consequently, we have

$$\tilde{G}_n = G_{n-2m},$$

and

$$\tilde{g}_n = g_{n-2m},$$

whenever $n \geq 2m$. (These quantities become 0 when $n < 2m$, but in our problem, n far exceeds $2m$). Therefore the number to be determined is $(1/n) \cdot (\tilde{g}_n / \tilde{G}_n) = (1/n) \cdot (g_{n-2m} / G_{n-2m})$. This lies between $1/6$ and $1/5$ whenever $n \geq 12 + 2m$. If m is a fixed quantity, then there is no change in the value of the limit.

$$\lim_{n \rightarrow \infty} (1/n) (\tilde{g}_n / \tilde{G}_n) = \lim_{n \rightarrow \infty} (1/n) (g_n / G_n).$$

If on the other hand m is not fixed, but only the ratio m/n is a fixed small quantity k , then because of the equality

$$(1/n) \cdot (\tilde{g}_n / \tilde{G}_n) = (1/n) \cdot (g_{n-2m} / G_{n-2m}) = (1-2k) (1/n-2m) (g_{n-2m} / G_{n-2m}),$$

the new value is $(1-2k)$ times the old value. Since k is usually small, the value is almost the same.

Let us illustrate the same in a few particular cases: When n is approximately 10^{20} and m is a fixed quantity (say, not more than 10^5), then the maximum yield is the same, viz, 82.3%. When n is approximately 10^{20} , and m is $10^{-10}n$, then the maximum yield lies between 82.3% and a quantity slightly more than this. Because this quantity coincides with 82.3 in the first few significant decimal places, one concludes that here again the value is virtually unchanged.

3.3 Comparison with other related work

The problem of how to determine the number of isolated single points when adjacent pairs are selected at random from a line of points has been of interest in a number of seemingly unrelated chemical studies and much has been written on this subject. Flory (1939) has used this mathematical concept in obtaining the fraction of functional substituents of vinyl polymers which may undergo reaction in pairs while Jackson and Montroll (1958) discuss the average concentrations of trapped free radicals condensed from gaseous mixtures onto surfaces cooled to liquid helium temperatures. Flory's (1939) model has been commented upon (Cohen and Reiss 1963) and other extensions have appeared (Littlewood and Verrall 1973). A more detailed study using difference equations has been carried out (Page 1959). We wish to compare our study with these methods.

In the work of Flory (1939) and Page (1959), a mathematical modelling different from ours has been considered. These studies take into account the extra factor of 'the sequence in which the reactions among the molecules take place'. In our treatment, on the other hand, this order is immaterial. Since the present understanding of the factors which control the initiation and progress of organic solid state reactions is not well-developed, it is difficult to decide which of these two situations is the more appropriate.

In either case, the observed experimental values of the extent of reaction in different β -cinnamic acids show considerable variation from the calculated values of 13% and 18% respectively of unreacted starting material.

Not only are the final answers different in the two cases, but the differences crop up for even small values of n . As a representative example, our value of g_5/G_5 is 6/4, but the value of the corresponding quantity S_5 is 16/15 according to Flory. There are two reasons for such a difference. First, as stated above, while counting the n -configurations, the sequence of reactions is taken into account. A configuration such as $\text{---} \text{---} \cdot$ would have been counted only once in G_5 but twice in S_5 since the initial relation could be either between the first and second points ($\text{---} \text{---} \cdot$) or between the third and fourth points ($\text{---} \text{---} \cdot$). So if the sequence of joining the points is important, there are more ways in which the configurations may be achieved. Secondly, Flory breaks up this aggregate of n -configurations into n parts, computes the average number of these isolated points separately in each of these parts, and finally takes the average of these averages to obtain S_n . Since the n parts are not of equal size, his S_n is different from the actual average of isolated points in these configurations.

Thus, because of a different assumption, and a different way of computing the averages, Flory's calculations are simpler than ours. In the paper by Page (1959) also, the first equation $p_{i,n} = p_i p_{n-i}$ is incorrect, as one can actually verify that $p_{3,5} = 1/6$ and $p_2 = 0$. For a similar reason as the one stated in the previous paragraph, his formula

$$p_n = (p_1 + \dots + p_{n-2})/(n-1)$$

is not correct. In fact, direct computations yield that

$$p_1 = 1; p_2 = 0; p_3 = 1/2; p_4 = 1/3; \text{ and } p_5 = 1/3,$$

where p_n is the probability that the left end point of an n -configuration is vacant. Here it is seen that p_5 is not equal to $(p_1 + p_2 + p_3)/4$. These observations necessitate a thorough calculation, similar to the one we have carried out in §§2.3 and 2.4.

The work of Jackson and Montroll (1958) (which we became aware of at a late stage) is closer to ours because it starts with the same set of mathematical assumptions and arrives at the same result. But three facts deserve mention here. First, the two approaches agree only in the initial step of framing the recurrence relations; later they are entirely different. Secondly our arguments in §2.3 are conceptually very simple unlike those of Jackson and Montroll. Even without solving the recurrence relations we have been able to decisively conclude, merely by means of simple inequalities, that the required probability lies between 81.72 and 82.31%. Further our method shows easily that for all values of $n \geq 19$, the required probability deviates from the limiting value by less than 0.6%. Finally, even while calculating the exact limit in §2.4, the two methods are quite distinctive. Our answer is in terms of the unique real root of $1 - x^2 - x^3$ whereas the result in the paper of Jackson and Montroll is in terms of the largest root of $x^3 - x - 1$.

4. Conclusion

It has been shown that the maximum possible theoretical conversion of β -cinnamic acid crystals to β -truxinic acid through a solid state topochemical photodimerisation process is around 82%. The recurrence relations that have been used to obtain this

result may also be employed to describe the situations where preferential reaction occurs near the crystal surfaces.

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Rotational isomerism and barriers to internal rotation in 3-halopropenes by SCF-MO methods

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Abstract. Electronic structures of 3 halopropenes have been investigated through semi-empirical SCF-MO calculations using valence basis sets of atomic orbitals (AO) constructed from Slater type orbitals (STO). The electronic structures of stable conformers have been predicted and the corresponding calculated dipole moments show good agreement with experimental data. The considerable differences between the dipole moments of various conformers confirm the hindrance to internal rotation about the C–C bond, i.e., the existence of a definite potential barrier to rotation. The barrier heights hindering the internal rotation in each system are also estimated.

Keywords. CNDO/2 and INDO methods; 3-halopropenes; barrier heights; internal rotation; dipole moment.

1. Introduction

In the last few years, there has been a great deal of interest in understanding the structural features of 3-halopropenes and most of the attempts in this direction are based on experimental methods such as electron diffraction in the gas phase (Schei and Shon 1982) proton magnetic resonance spectral studies (Bothner-by *et al* 1965, 1966), microwave spectral studies (Hirota 1965, 1970), etc. Theoretical investigations on the conformations of these systems are very much limited mainly because of the large computation time involved in such calculations. The structural features of 3-fluoropropene (3FP) have been reported following the full *ab initio* SCF-MO calculations using minimal basis sets of atomic orbitals 7s, 3p (for C, O and F) and 3s (for H) Gaussian functions (Cadioli and Pincelli 1972). In the present theoretical study, SCF-MO calculations at INDO (intermediate neglect of differential overlap) and CNDO (complete neglect of differential overlap) levels of approximations have been performed for 3-chloropropene (3CIP), 3-bromopropene (3BrP) and 3-iodopropene (3IP), using both *spd* (s, p and d valence functions) and *sp* (s and p valence functions only) basis sets. The reason for resorting to semi-empirical methods rather than full *ab initio* calculations, is to save computation time, which would normally be very high for *ab initio* type calculations, especially when heavy atoms such as bromine and iodine are involved. Calculations on 3FP have also been performed at the same levels of approximation and the results have been compared with both the experimental values and the predictions of full *ab initio* calculations to ascertain the accuracy of the semi-empirical methods adopted in the present investigations. Thus the aim of the present study is two-fold:

(a) to identify the stable conformers and to estimate the barrier heights to internal rotation about the C–C bond;

(b) to establish the validity and the applicability of INDO and CNDO semi-empirical methods in these calculations.

2. Method of calculation

The calculations have been performed following Roothan's SCF scheme based on the Hartree-Fock equation for a many electron system. Valence basis sets, comprising just those orbitals of the valence shell of each atom in the molecule are adopted in the present calculations and to construct such AO basis set, Slater type orbitals (STO) are used. Of all the semi-empirical schemes available in the literature for running MO calculations, the SCF-MO method developed by Pople and Beveridge (1970) in the approximations of INDO and CNDO are considerably more accurate. Thanks to the possibility of calculating the electronic populations of all the valence atomic orbitals, one can calculate all the components of the total molecular dipole moment and achieve very good agreement between the calculated and the experimental values of dipole moments. The earlier computer program based on Pople and Beveridge's CNDO/2 and INDO methods allow all-valence electron calculations for molecules containing only simple atoms such as hydrogen and the elements of the first and second rows of the periodic table. Subsequently the formula for calculating molecular dipole moment by CNDO/2 method has been extended (Hase and Schweig 1973) to cover molecules containing elements of the third row of the periodic table. In the earlier work (Santhanam and Sobhanadri 1985) the authors have succeeded in extending the scheme to cover molecules containing elements of the fourth row as well and the same programme has been adopted for performing calculations on 3IP.

3. Computations, results and discussion

In calculations performed for 3FP, 3CIP, 3BrP and 3IP, experimental bond distances and bond angles of the *cis* form (figure 1) are used (refer table 1) (Sutton 1965). SCF total energies and the dipole moments have been calculated for selected values of the torsional angle α and the results collected in tables 2-6. The values of the dipole moments for various conformers in each system differ substantially from each other, indicating that all the possible isomers produced by internal rotation are not

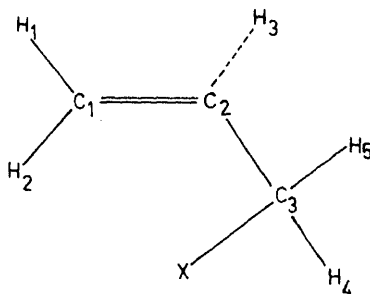


Figure 1. *s*-Cis-3-halopropene ($\alpha = 0^\circ$); X = F, Cl, Br, I.

Table 1. Bond distances for the *cis* form in Å.

C(1)=C(2) = 1.34	C(3)-H(5) = 1.09
C(2)-C(3) = 1.52	C(3)-F = 1.36
C(1)-H(1) = 1.08	C(3)-C1 = 1.795
C(1)-H(2) = 1.08	C(3)-Br = 2.00
C(2)-H(3) = 1.08	C(3)-I = 2.18
C(3)-H(4) = 1.09	

Table 2. INDO and CNDO total energies ($E/a.u.$) and dipole moments (μ/D) for 3FP for selected values of the torsional angle (*spd* basis set).

		Torsional angle, α			
Method		0°	60°	120°	180°
INDO	<i>E</i>	-50.67982	-50.67610	-50.67689	-50.67749
	μ	1.84	1.83	1.91	1.79
CNDO	<i>E</i>	-52.74805	-52.74389	-52.74447	-52.74533
	μ	1.82	1.76	1.79	1.64

Table 3. INDO and CNDO total energies ($E/a.u.$) and dipole moments (μ/D) for 3ClP for selected values of the torsional angle (*spd* basis set).

	Torsional angle, α				
Method	0°	60°	120°	180°	
INDO	<i>E</i>	-39.51736	-39.51222	-39.51363	-39.51124
	μ	2.04	1.97	2.02	1.96
CNDO	<i>E</i>	-41.17606	-41.17065	-41.17175	-41.16942
	μ	1.86	1.72	1.68	1.64

Table 4. INDO and CNDO total energies ($E/a.u.$) and dipole moments (μ/D) for 3BrP for selected values of the torsional angle (*spd* basis set).

		Torsional angle, α			
Method		0°	60°	120°	180°
INDO	<i>E</i>	-36.79063	-36.77415	-36.77477	-36.77126
	μ	2.31	2.02	2.00	2.02
CNDO	<i>E</i>	-38.35380	-38.33735	-38.33762	-38.33398
	μ	2.22	1.75	1.61	1.66

Table 5. INDO and CNDO total energies ($E/a.u.$) and dipole moments (μ/D) for 3IP for selected values of the torsional angle (*spd* basis set).

		Torsional angle, α			
Method		0°	60°	120°	180°
INDO	<i>E</i>	-36.23769	-36.22922	-36.23098	-36.22683
	μ	0.51	0.25	0.25	0.22
CNDO	<i>E</i>	-37.68140	-37.67283	-37.67421	-37.67003
	μ	0.01	0.39	0.53	0.44

Table 6. INDO and CNDO total energies ($E/a.u.$) and dipole moments (μ/D) for 3IP for selected values of the torsional angle (*sp* basis set).

		Torsional angle, α			
Method		0°	60°	120°	180°
INDO	<i>E</i>	-36.14842	-36.14888	-36.15217	-36.14765
	μ	1.86	1.74	1.78	1.79
CNDO	<i>E</i>	-37.58692	-37.58733	-37.59035	-37.58579
	μ	1.47	1.23	1.15	1.20

energetically equivalent and hence, the necessity for taking into account the potential energy of internal rotation in calculations of the mean dipole moment for each temperature. Results of the full *ab initio* calculations (Cadioli and Pincelli 1972) indicate the existence of two stable conformers for 3FP, one at $\alpha = 0$ and the other at $\alpha = 130^\circ$ with an energy difference of 1.17 kcal/mole between them. Experimental study predicts the same trend, but the second conformer corresponds to an α value of 127° and the energy difference between the two stable conformers is as low as 0.31 kcal/mole. In the present study, the INDO potential curve for 3FP, as shown in figure 2, predicts the existence of two stable conformers one at $\alpha = 0^\circ$ and the other at $\alpha = 160^\circ$ with an energy separation of 1.45 kcal/mole between them. Two distinct barriers to internal rotation, a *cis*-gauche barrier at $\alpha = 68^\circ$ with a height of 2.89 kcal/mole and a *gauche-trans*-gauche barrier at a height 0.82 kcal/mole above the 130° energy have been reported for 3FP by full *ab initio* calculation. The present INDO calculations on 3FP lead to a value of 2.7 kcal/mole for the first potential barrier and the second *gauche-trans*-gauche barrier is not well defined at this level of approximation (figure 2). Experimental observation (Meakin *et al* 1969) indicated the existence of a first potential barrier at 3.11 kcal/mole and the second at 1.46 kcal/mole. As regards the dipole moment, the calculated INDO values agree quite well with the experimental figures. For example, the INDO values of dipole moment of 3FP in the *cis* and 120° *gauche* forms are 1.84D and 1.91D which compare favourably with the Stark effect values of 1.77D and 1.94D respectively. The corresponding values from the *ab initio* calculations are 1.91D and 2.12D respectively. It appears therefore that SCF-MO formalism working within the

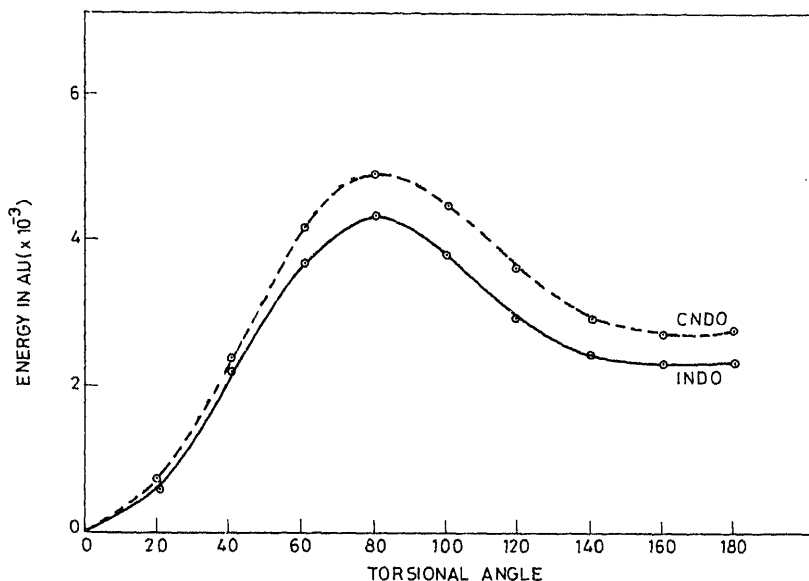


Figure 2. Energy versus torsional angle curves for 3FP (zero reference corresponds to the *cis*-form).

framework of INDO level approximation along with the chosen basis set can give reliable results in molecular calculations.

Similar analysis has been carried out from the results of the calculations performed for 3ClP, 3BrP and 3IP and stable isomers have been identified in terms of the total molecular energy.

In the case of 3ClP, stable conformers have been found at α values 0° and 120° with an energy difference 2.35 kcal/mole by the INDO method and 2.37 kcal/mole by the CNDO method (figure 3). The *cis*-gauche and gauche-*trans*-gauche barriers to internal rotation have been found with peak heights 3.23 kcal/mole and 3.85 kcal/mole respectively by the INDO method. Calculated dipole moments for various conformers of 3ClP by the INDO method range from 1.96D to 2.04D (table 3) which compare reasonably well with the experimental range of 1.90D and 2.40D (Hannay and Smyth 1946; Trinh 1949). Dipole moments obtained from CNDO calculations have also been given for the sake of comparison.

For 3BrP also two stable conformers with α values 0° and 120° have been identified but the energy difference between them is pretty high (9.9 kcal/mole). Here again two distinct barriers with peak values 10.7 kcal/mole and 12.2 kcal/mole have been observed (figure 4). The range of the dipole moments for various conformers is found to be 1.99D to 2.31D which falls a little away from the experimental value of 1.82D cited in the literature (Rogers and Panish 1955).

Calculations on 3IP revealed almost the same trend as in other halopropenes but the dipole moments for all the conformers are very poorly estimated. Two stable

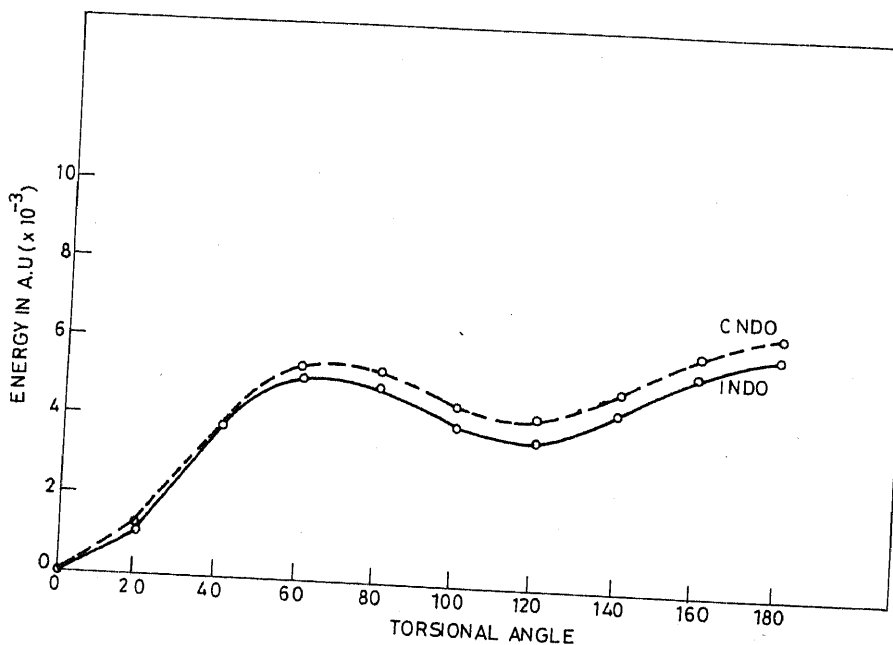


Figure 3. Energy versus torsional angle curves for 3 CIP (zero reference corresponds to the *cis*-form).

and 2.82 kcal/mole above 100° energy by INDO and CNDO methods respectively. The calculated dipole moments for various conformers are as low as 0.5D, which is very small compared to the experimental value of 1.62D (Rogers and Panish 1955). The above results are obtained from calculations using *spd* valence basis set. On the other hand, when the calculations are repeated using only *s* and *p* valence orbitals (*sp* basis set) the dipole moments for various conformers improve very nicely but the profile of the energy versus torsional angle curve is completely reversed (figure 6).

This graph clearly indicates that in the case of 3IP, the *gauche* form is more stable than the *cis* form. Energy versus torsional angle curves shown in figures 2–5 have been drawn using energy values calculated using *spd* basis set. From all these curves, it is clear that for all halides, the *cis* form is energetically more favourable than the *gauche* form. But the high resolution proton NMR spectral studies (Bothner-by and Gunther 1962; Govil 1966) show that in 3CIP itself, there is some preference for the *gauche* form rather than the *cis* form and this tendency is much pronounced in the case of 3BrP and 3IP. This fact has been confirmed quite recently from electron diffraction study in the gas phase on 3BrP (Schei and Shen 1982) wherein it is reported that the population of the *gauche* form is as high as 95%. In the present study, the MO calculations carried out with the *sp* basis set on 3IP reveals this experimental trend unambiguously.

Inclusion of *d*-orbitals in the basis set should generally improve the accuracy of the calculation of molecular properties at the loss of simple pictorial description of the molecular orbitals (Galasso 1974) and several authors (Svendsen and Stroyer-Hansen 1978; Teixeira-Dias and Mursell 1970; Teixeira-Dias and Saree 1975; Facelli and Contreras 1980) have realized the need to introduce such polarization functions into

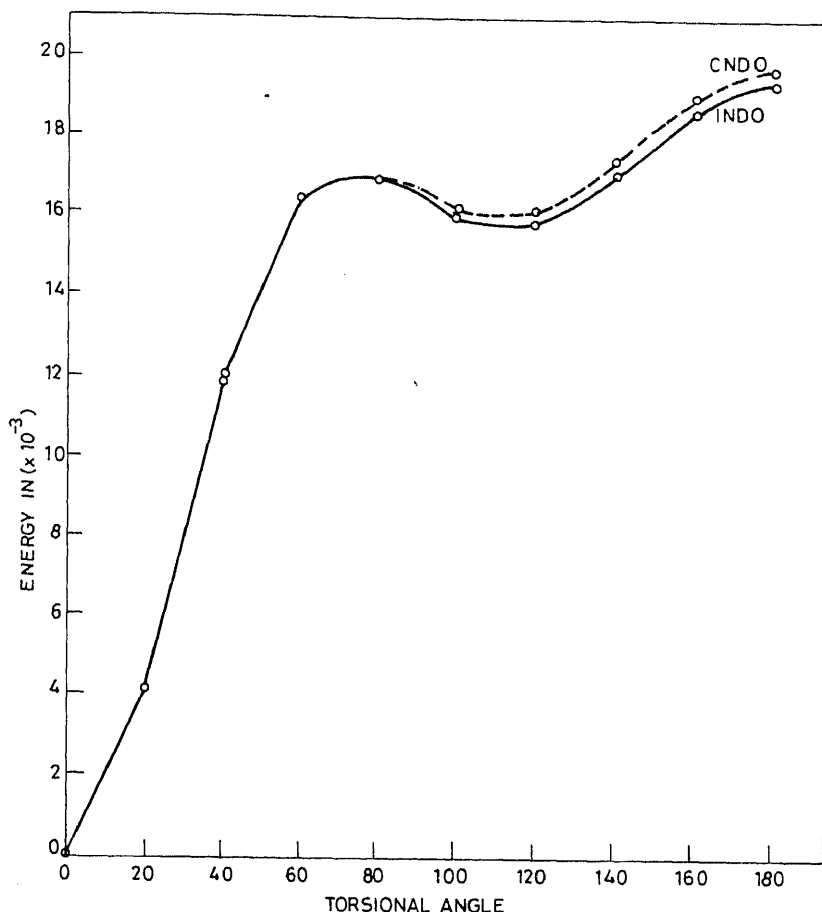


Figure 4. Energy versus torsional angle curves for 3 BrP (zero reference corresponds to the *cis*-form).

the basis set to improve the calculation. The reason for the very poor performance of the *d* orbitals in the present calculation could be that the energy gap between the *p* and *d* valence orbitals in the case of heavy elements is very large and hence if one could make a provision to include the intermediate orbitals (lying between *p* and *d* valence orbitals) also in the calculation, the results might improve satisfactorily (Santhanam and Sobhanadri 1985). This requires some provision for the mixing of orbitals with different principal quantum numbers. Also the lack of a better parameterization scheme, especially for heavy elements, could be another reason for such a poor show of the *d* orbitals in the present investigation.

On the other hand, the experimental findings of the most stable conformers for 3FP are replicated by the present calculations. Most of the main features of the potential energy curves drawn between the total energy and the torsional angle for all the halides have been satisfactorily reproduced even though the basis set is relatively small (6-31G).

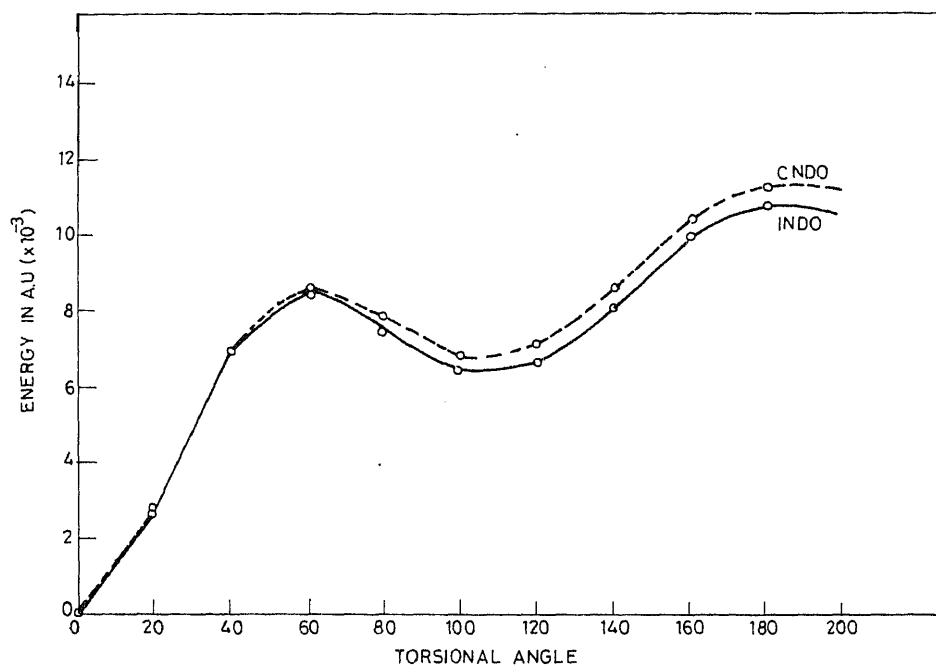
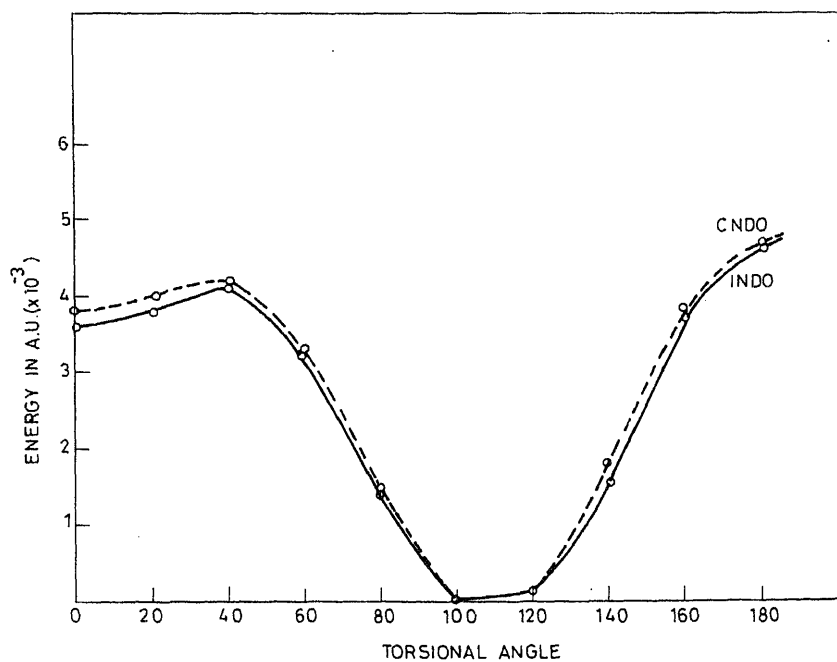


Figure 5. Energy versus torsional angle curves for 3IP (zero reference corresponds to the *cis*-form).



validity of the approximations that are inherent in the INDO and CNDO semi-empirical SCF-MO schemes. It must also be realised at this point that the results presented here are obtained by a rigid rotation of the CH_2X group, without allowing for any geometrical relaxation with respect to the bond parameters of the *cis* form. The importance of such geometric relaxation has been felt and stressed by many authors (Veillard 1970). Also it should be mentioned that even though the independent particle model (Veillard 1970; Fink and Allen 1967; Allen 1968) could satisfactorily account for the most hindered internal rotations about pure single bonds one should explicitly include the electron correlation effects for reducing the SCF energy separation between the two stable conformers of the molecules.

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The scaled one-electron Hamiltonian model for open-shell LCAO-MO-SCF calculations: further corrections to the SOEH energy

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Abstract. The wavefunction generated by the scaled one-electron Hamiltonian (SOEH) model has been modified further by including all single excitations from the space of the SOEH function. A perturbation-variation ansatz has been invoked for obtaining the corresponding energy correction (ΔE_2). $[E(\text{SOEH}) + \Delta E_2]$ is shown to reproduce $E(\text{Roothaan})$ very closely. It has been demonstrated that by making ΔE_2 stationary with respect to change in μ , an approximate analytical expression for the theoretical calculation of the scaling parameter μ results. The corrected SOEH $[E(\text{SOEH}) + \Delta E_2]$ is shown to be quite useful for the calculation of geometrical parameters of open-shell systems even though it lacks the 'upper-boundedness' exhibited by $E(\text{SOEH})$.

Keywords. Open-shell SCF calculations; average Hamiltonian model; scaled one-electron Hamiltonian model; variation-perturbation calculation; second order energy correction.

1. Introduction

Recently, we have proposed a scaled one-electron Hamiltonian (SOEH) model for performing restricted open-shell calculations at an approximate level and tested its performance (Bhattacharyya 1981; Bhattacharyya and Chowdhury 1981; Banerjee and Bhattacharyya 1982). We may recall that the SOEH model belongs to the class of methods called the average Fock-operator models (Nesbet and Watson 1960; Nesbet 1961, 1963; Dewar *et al* 1968; Ellison and Matheu 1971; Carbo *et al* 1980) that have been suggested from time to time as expedient means of tackling the restricted open-shell Hartree-Fock problem for molecules in an approximate fashion. An evaluation of the performance pattern of our model (Banerjee and Bhattacharyya 1982) vis-a-vis that of the restricted open-shell method of Roothaan (1960) has shown that the SOEH model can be profitably utilised for structural investigations on open-shell molecular species at least at the semiempirical level of approximation (the method is yet to be tested in an *ab initio* framework). In fact, in all the cases investigated (Banerjee and Bhattacharyya 1982) the electronic energy calculated by the SOEH model was just slightly (0.005 a.u. on the average) above the energy calculated by Roothaan's procedure and thus appeared (was not demonstrated analytically) to have an upperbound character as it never shot below the energy calculated by the latter procedure. Needless to mention the energy estimated by the method of Roothaan itself is a variational upperbound to the exact energy.

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parameter μ in the exchange part of the total energy in a Hartree-Fock like scheme, applying variational argument to the scaled pseudo-energy functional and, thereby generating a pseudo-Hartree-Fock like operator (F^{av}) which contains the scaling parameter (μ) explicitly as a multiplicative factor in the exchange operator (K_m) for the open-shell electron assigned to the orbital ϕ_m (say). In our previous studies we had interpreted μ as a mere averaging factor, the averaging process being applied to the exchange potential contributed by the closed- and the open-shell electrons. One may, however, look for an alternative rationalization of the parameter concerned. The present communication is a sequel to an afterthought of this kind. The strategy adopted for the projected investigation is straightforward. We use the orbitals generated by the SOEH model to construct the ground state wavefunction (ψ_0^{av}) and then modify this function by adding all single excitations from the doubly and singly occupied manifolds. The corresponding energy correction along with the amplitudes of various single excitations are determined by making use of a simple variation perturbation ansatz. The energy correction (ΔE_2) is an explicit as well as an implicit function of the scaling parameter μ . Accordingly making $\Delta E_2(\mu)$ stationary with respect to variation in the scaling parameter (i.e., by setting $\partial \Delta E_2 / \partial \mu = 0$), leads to an approximate analytical expression for μ (we call it μ_0). The energy correction ΔE_2 when added to the SOEH energy $E(\text{SOEH})$ (for a given scale factor μ) recovers, in most of the cases, the energy estimated by the RHF methodology of Roothaan (1960). But as ΔE_2 is not expected to have any 'upper-bound' character, the sum $[E(\text{SOEH}) + \Delta E_2]$ may even shoot below $E(\text{Roothaan})$ (see later). Even then we expect $[E(\text{SOEH}) + \Delta E_2]$ to remain very close to $E(\text{Roothaan})$, an expectation which is found to be correct in actual numerical calculations.

The outline of the paper is as follows. In §2 we develop our method and arrive at an analytical expression for ΔE_2 . We also attempt to rationalize the meaning of the μ parameter in the same context (§3). In §4.1 we have investigated the variation of $\Delta E_2(\mu)$, $[E(\text{SOEH}) + \Delta E_2]$ for various starting orbitals chosen. We may note here that the use of a specific value of μ in F^{av} determines a specific set of initial orbitals. The relative performances of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2(\mu)]$ vis-a-vis $E(\text{Roothaan})$ in the calculation of geometrical features of a doublet radical in the ground state is discussed in §4.2 while §5 summarises the main findings of the present investigation.

2. Analytical expression for ΔE_2

Before setting out to derive an analytical expression for ΔE_2 we will first clarify our notations. The set $\{\phi_i\} i = 1, n_d$ represents the collection of doubly occupied orbitals, $\{\phi_m\} m = 1, n_o$, the singly occupied orbitals and $\{\phi_p\} p = 1, n_v$ the so-called virtual manifold, all generated by the SOEH (F^{av}) which contains the scaling-parameter μ . The corresponding eigenvalues are given by the sets $\{\epsilon_i\} i = 1, n_d$, $\{\epsilon_m\} m = 1, n_o$ and $\{\epsilon_p\} p = 1, n_v$ respectively. Let ψ_0^{av} represent the wavefunction for the doublet state of the open-shell system under consideration as envisaged in the SOEH model and let the 'corrected' wavefunction for the same state, after the inclusion of the 'specified' singly excited configurations (singly excited with respect to ψ_0^{av}) be $\tilde{\psi}_0$. Then (assuming a single open-shell orbital designated by ϕ_m) we have

$$\tilde{\psi}_0 = \psi_0^{\text{av}} + \sum_{i=1}^{n_d} C_{im} \psi_{im} + \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip} \psi_{ip} + \sum_{p=1}^{n_v} C_{mp} \psi_{mp}, \quad (1)$$

$$\psi_0^{\text{av}} = |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_i \dots \phi_m|; \psi_{im} = |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_m \dots \phi_m|;$$

$$\psi_{ip}(s=0) = \frac{1}{\sqrt{2}} \{ |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_p \dots \phi_m| - |\phi_1 \bar{\phi}_1 \dots \bar{\phi}_i \phi_p \dots \phi_m| \};$$

$$\psi_{mp} = |\phi_1 \bar{\phi}_1 \dots \phi_i \bar{\phi}_i \dots \phi_p|;$$

where $\psi_{ij}(S=0)$ merely denotes that the $\phi_i \rightarrow \phi_j$ excitation is a singlet spin-coupled one. One notes here in the passing that the configuration functions are built up from the orbitals generated by the SOEH model with a given value of μ .

Using $\tilde{\psi}_0$ defined by (1) as the trial wavefunction

$$E(\tilde{\psi}_0) = \langle \tilde{\psi}_0 | H | \tilde{\psi}_0 \rangle / \langle \tilde{\psi}_0 | \tilde{\psi}_0 \rangle. \quad (2)$$

Substituting (1) in (2) and retaining terms only upto the second order of magnitude, we have

$$\begin{aligned} E(\tilde{\psi}_0) = & E(\psi_0^{\text{av}}) + 2\mu \sum_{i=1}^{n_d} C_{im} \langle \phi_i \phi_m | \phi_m \phi_m \rangle \\ & + \sum_{i=1}^{n_d} C_{im}^2 \{ \varepsilon_m - \varepsilon_i - J_{im} + \mu K_{mm} + (1-\mu) K_{im} \} \\ & + 2(\mu-1) \sum_{p=1}^{n_v} C_{mp} \langle \phi_p \phi_m | \phi_m \phi_m \rangle \\ & + \sum_{p=1}^{n_v} C_{mp}^2 \{ \varepsilon_p - \varepsilon_m - J_{mp} + \mu K_{mp} + (1-\mu) K_{mm} \} \\ & + 2\sqrt{2} (\mu - \frac{1}{2}) \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip} \langle \phi_i \phi_m | \phi_p \phi_m \rangle \\ & + \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} C_{ip}^2 \{ \varepsilon_p - \varepsilon_i - J_{ip} + 2K_{ip} - (\mu - \frac{1}{2}) K_{im} + (\mu - \frac{1}{2}) K_{pm} \}. \quad (3) \end{aligned}$$

To arrive at (3), use has been made of the fact that the orbitals used in the construction of all the configuration functions are eigenfunctions of the SOEH operator (F^{av}) where,

$$F^{\text{av}} = h(1) + \sum_{i=1}^{n_d} (2J_i - K_i) - J_m - \mu K_m. \quad (4)$$

In general, therefore, $F^{\text{av}} \phi_i = \varepsilon_i \phi_i$; where ϕ_i belongs to the doubly occupied, singly occupied or unoccupied manifolds. By way of clarifying the notations further, we may note here that

$$J_{ij} = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_i(1) \phi_j(2) dv_1 dv_2$$

$$K_{ij} = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_j(1) \phi_i(2) dv_1 dv_2,$$

and

$$\langle \phi_i \phi_j | \phi_k \phi_i \rangle = \iint \phi_i(1) \phi_j(2) r_{12}^{-1} \phi_k(1) \phi_i(2) dv_1 dv_2.$$

Now making the functional in (3) stationary with respect to various coefficients

appearing in (3) we arrive at

$$C_{im} = \frac{\mu \langle \phi_i \phi_m | \phi_m \phi_m \rangle}{\{\varepsilon_m - \varepsilon_i - J_{im} + K_{im}(1 - \mu) - \mu K_{mm}\}}, \quad (5)$$

$$C_{ip} = -\frac{\sqrt{2}(\mu - \frac{1}{2}) \langle \phi_i \phi_m | \phi_p \phi_m \rangle}{\{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} - J_{ip} + 2K_{ip} + \frac{1}{2} K_{im}\}}, \quad (6)$$

$$C_{mp} = -\frac{(\mu - 1) \langle \phi_m \phi_m | \phi_m \phi_m \rangle}{\{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\}}. \quad (7)$$

Now substituting the values of the set of coefficients (C_{im}), (C_{ip}) and (C_{mp}) as given by (5) to (7) in (3), we arrive at the corrected expression for the SOEH energy after some trivial manipulations:

$$\begin{aligned} E(\tilde{\psi}_0) &= E(\psi_0^{\text{av}}) - \mu^2 \sum_{i=1}^{n_d} \langle \phi_i \phi_m | \phi_m \phi_m \rangle^2 / \{\varepsilon_m - \varepsilon_i - J_{im} + (1 - \mu) K_{im} - \mu K_{mm}\} \\ &\quad - (\mu - 1)^2 \sum_{p=1}^{n_v} \langle \phi_m \phi_m | \phi_m \phi_p \rangle^2 / \{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\} \\ &\quad - 2(\mu - \frac{1}{2})^2 \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} \langle \phi_i \phi_m | \phi_p \phi_m \rangle^2 / \{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} \\ &\quad + 2K_{ip} + \frac{1}{2} K_{im}\}. \end{aligned} \quad (8)$$

The correction to the SOEH energy, therefore turns out to be (at the level of approximation used by us) as follows

$$\Delta E_2 = E(\tilde{\psi}_0) - E(\psi_0^{\text{av}}) = -\mu^2 X - (\mu - 1)^2 Y - 2(\mu - \frac{1}{2})^2 Z \quad (9)$$

where

$$\begin{aligned} X &= \sum_{i=1}^{n_d} \langle \phi_i \phi_m | \phi_m \phi_m \rangle^2 / \{\varepsilon_m - \varepsilon_i - J_{im} + (1 - \mu) K_{im} - \mu K_{mm}\}, \\ Y &= \sum_{p=1}^{n_v} \langle \phi_m \phi_m | \phi_m \phi_p \rangle^2 / \{\varepsilon_p - \varepsilon_m + \mu K_{mp} - J_{mp} - (\mu - 1) K_{mm}\}, \\ Z &= \sum_{i=1}^{n_d} \sum_{p=1}^{n_v} \langle \phi_i \phi_m | \phi_p \phi_m \rangle^2 / \{\varepsilon_p - \varepsilon_i + (\mu - \frac{1}{2}) K_{pm} + 2K_{ip} + \frac{1}{2} K_{im}\}. \end{aligned}$$

3. Approximate analytical expression for μ_0

We can write the corrected SOEH energy in the following series:

$$\begin{aligned} E &= (E_0 + \Delta E_1) + \Delta E_2 + \Delta E_3 + \dots \\ &= E(\text{SOEH}) + \Delta E_2 + \Delta E_3 + \dots \end{aligned} \quad (10)$$

Let us assume now that $E(\text{SOEH})$ has been calculated by using the values of μ obtained by brute-force optimization of $E(\text{SOEH})$ as a function of μ . So the $E(\text{SOEH})$ part of the energy series represented by (10) must be stationary with respect to further variation in μ . Hence, for this particular choice of reference point for the perturbation

$$\begin{aligned}\frac{\partial E}{\partial \mu} &= \frac{\partial E(\text{SOEH})}{\partial \mu} + \frac{\partial}{\partial \mu} (\Delta E_2) + \frac{\partial}{\partial \mu} (\Delta E_3) + \dots \\ &= 0 + \frac{\partial}{\partial \mu} \{ \Delta E_2 + \Delta E_3 + \dots \} \simeq \frac{\partial}{\partial \mu} (\Delta E_2)\end{aligned}\quad (11)$$

assuming of course that the energy series in (10) converges. Hence, for the given choice of reference point the condition $\partial E/\partial \mu = 0$ is equivalent to demanding

$$\partial \Delta E_2 / \partial \mu = 0. \quad (12)$$

Since, ΔE_2 is given by (9), (12) leads us to,

$$\mu_0 = (Z + Y)/(X + Y + 2Z). \quad (13)$$

If we use some other reference energy [i.e., other than $E(\text{SOEH})$ calculated by $\mu = \mu_0$ (brute-force)] which is not far off from the optimum reference energy (13) still remains approximately valid. This is because the variation of $E(\text{SOEH})$ with μ (in the neighbourhood of $E(\text{SOEH})_{\text{optimum}}$) has been generally found to be very slow (Bhattacharyya 1981; Banerjee and Bhattacharyya 1982). Hence, setting $(\partial E/\partial \mu)(\text{SOEH}) = 0$ will be approximately valid even for non-optimum reference energy also. It may be mentioned here that a slightly better value of μ correct to second order could be estimated in principle by using (13) to calculate μ for a given set of starting orbitals, putting it back in F_{av} in (4) and iterating until a self-consistent value of μ is obtained. However, this would have increased the computational requirement considerably as many two-electron integrals would have to be recalculated at each scf cycle. This scf-perturbation approach was not therefore attempted by us.

A question to ponder over here is whether the μ_0 calculated by (13) should be identical with the μ_0 calculated by the brute-force optimization of $E(\text{SOEH})$ alone? The answer is clearly in the negative since $(\partial E/\partial \mu)(\text{SOEH}) = 0$ does not mean that higher order corrections ($\Delta E_2, \Delta E_3$ etc.) are all zero. Thus, the present μ_0 corresponds to minimization of $[E(\text{SOEH}) + \Delta E_2]$ while the previous one was determined by the minimization of $E(\text{SOEH})$ alone. The two conditions are therefore not identical.

4. Results and discussion

4.1 Dependence of ΔE_2 on the choice of the starting orbitals

We have already noted at the outset that the scaling parameter μ occurs explicitly in the SOEH operator [viz, (4)] and therefore, different choices of μ will naturally generate different sets of initial orbitals for construction of the various configuration functions appearing in (1). It is therefore imperative to explore the μ -dependence of the calculated values of ΔE_2 as given by (9). In other words, this amounts to testing how sensitive the calculated values of ΔE_2 are to variations in the orbital basis-set used in the construction of the configuration functions in terms of which ψ_0 is expanded (1).

Table 1 summarises the results obtained for the 9 valence electron CN radical ($r_{\text{CN}} = 1.172 \text{ \AA}$) using the standard CNDO/2 parameters (Pople *et al* 1965). We have employed a wide range of values of μ (from 0.10 to 0.70 in steps of 0.05). In the present

Table 1. The pattern of variation of the SOEH energy and the corrected SOEH energy $[E(\text{SOEH}) + \Delta E_2]$ with changes of the scaling parameter μ observed for the ground state of the CN radical ($r_{\text{CN}} = 1.172\text{\AA}$)*. The calculated values of μ_0 are also reported.

Values of μ used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)	μ_0 (calculated)
0.10	-27.14544	-27.14549		0.2213
0.15	-27.14560	-27.14565		0.2215
0.20	-27.14579	-27.14583		0.2207
0.25	-27.14595	-27.14599		0.2199
0.30	-27.14607	-27.14611	-27.146363	0.2190
0.35	-27.14616	-27.14620		0.2181
0.40	-27.14622	-27.14627		0.2173
0.45	-27.14626	-27.14632		0.2165
0.50	-27.14628	-27.14635		0.2157
0.55	-27.14628	-27.146361		0.2149
0.60	-27.14624	-27.14633		0.2136
0.65	-27.14615	-27.14625		0.2124
0.70	-27.14605	-27.14616		0.2114

* Bond length from Sutton (1958).

case, the magnitude of ΔE_2 is very small but even then a 'soft' μ -dependence of ΔE_2 is discernible. One may notice further that while $E(\text{SOEH})$ as a function of μ shows up a flat minimum around $\mu = 0.50$ to 0.55 , the minimum of the modified SOEH energy i.e., the minimum of $[E(\text{SOEH}) + \Delta E_2]$ is a bit more prominent at $\mu = 0.55$. The minimum value of $[E(\text{SOEH}) + \Delta E_2] - 27.146361$ a.u. being admirably close to $E(\text{Roothaan})$ which is -27.146363 a.u. In this particular case neither $E(\text{SOEH})$ nor $[E(\text{SOEH}) + \Delta E_2]$ shoot below $E(\text{Roothaan})$. However, $[E(\text{SOEH}) + \Delta E_2]$ cannot, in general, be expected to show this kind of upperboundedness, as ΔE_2 is not bounded.

In table 1, we have also included the values of μ_0 calculated by using (13) for different sets of orbitals generated by F^{av} with different values of the scaling parameter μ . It is clear that the calculated values of μ_0 weakly depends on the choice of initial orbitals as revealed by the soft μ -dependence of the calculated value of μ_0 . One may note in this connection that our standard choice of $\mu = n_\alpha/(n_\alpha + n_\beta)$ leads to the value of $\mu = 0.5555$ in the present case while the μ_0 value predicted by our model turns out to be rather small ($\mu_0 = 0.21$). As mentioned earlier, this is expected as this possibly reflects the necessity of including still higher order excitations in (1) in order to predict reliable values of μ_0 . In other words the analytical structure of μ_0 appears to be far more involved than envisaged in the present model. The value of $[E(\text{SOEH}) + \Delta E_2]$ for $\mu = 0.5555$ is -27.14622 a.u., quite close to the value of $E(\text{Roothaan})$ (see table 1) which tends to suggest that in most of the cases $[E(\text{SOEH}) + \Delta E_2]$ corresponding to our standard choice μ will approximate $E(\text{Roothaan})$ sufficiently closely.

Table 2 summarises the results obtained for BF_2 (17 valence electrons, FBF

Table 2. The pattern of μ -dependence displayed by $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in $\text{BF}_2(r_{\text{BF}} = 1.3 \text{ \AA}, \text{F-B-F} = 124.6^\circ)^*$.

μ -values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.0	-87.06303	-87.06313	
0.1	-87.06315	-87.06322	
0.2	-87.06329	-87.06334	
0.3	-87.06338	-87.06342	-87.063522
0.4	-87.06343	-87.06348	
0.5	-87.06345	-87.06352	
0.6	-87.06344	-87.06354	
0.7	-87.06333	-87.06348	

* Bond lengths and angles from Sutton (1958).

Table 3. The observed μ -dependence of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in $\text{NF}_2(r_{\text{NF}} = 1.35 \text{ \AA}, \text{F-N-F} = 139^\circ)^*$.

μ values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.00	-106.77401	-106.77949	
0.05	-106.77395	-106.77835	
0.10	-106.77383	-106.77732	
0.15	-106.77361	-106.77642	
0.20	-106.77330	-106.77565	
0.25	-106.77289	-106.77499	-106.77402
0.30	-106.77239	-106.77445	
0.40	-106.77107	-106.77363	
0.50	-106.76937	-106.77317	
0.60	-106.76731	-106.77285	

* Bond lengths and angles from Sutton (1958).

contrast, $E(\text{SOEH})$ is seen to remain slightly above $E(\text{Roothaan})$ for any value of μ chosen by us revealing its upperbound character (Bhattacharyya and Chowdhury 1981; Banerjee and Bhattacharyya 1982).

In table 3 we have presented the rather interesting results obtained with NF_2 (19 valence electrons, $\text{FNF} = 139^\circ$, $r_{\text{NF}} = 1.35 \text{ \AA}$). The calculated values of ΔE_2 reveal in this case quite a perceptible μ -dependence. As can be seen from the table, ΔE_2 as a function of μ shows up a clear minimum at $\mu = 0.30$. On the other hand, $E(\text{SOEH})$ itself attains its minimum value for $\mu = 0.0$. Recalling that $E(\text{SOEH})$ represents the energy correct upto the first order, we would have expected ΔE_2 also to be minimum for $\mu = 0.0$. However, that demands that the energy series be convergent for $\mu = 0.0$. Possibly, for $\mu = 0.0$ the higher order terms begin to make sizable contribution, so that the truncation of the energy series at ΔE_2 may lead to erroneous conclusions. On the other hand, by setting $\mu = n_a/(n_a + n_p)$ for the present systems also, the SOEH energy, as seen from the table concerned, provides quite a good reference point for the calculation of the first correction to the SOEH energy.

4.2 Geometry optimization with $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$

Since the inclusion of ΔE_2 improves the energy estimate considerably in most of the systems studied, it would be worthwhile to test the effect of including ΔE_2 on the optimization of the geometrical parameters of simple radicals. Earlier, we have demonstrated (Banerjee and Bhattacharyya 1982) the utility of the 'native' SOEH model in the computation of equilibrium geometries of simple radicals or ions within the limits of approximate orbital theories. As a test case for our present study, we have chosen the HCO radical and we propose to optimize the H-C-O angle keeping r_{CH} and r_{CO} fixed at their experimental values (1.08 Å and 1.198 Å respectively).

Before proceeding to present results of geometry optimization of the HCO radical we will first discuss the results of a 'brute force' optimization of μ for H-C-O at a fixed geometry (viz, $r_{\text{CH}} = 1.08$ Å, $r_{\text{CO}} = 1.198$ Å, $\text{HCO} = 120^\circ$). The pertinent results are presented in table 4. One may easily see from the table concerned that both $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ attains minima for $\mu = 0.55$. We therefore used $\mu = 0.55$ in all our subsequent calculations pertaining to the optimization of the HCO angle in the HCO radical [note that $n_\alpha/(n_\alpha + n_\beta) = 0.5454$]. The results of these calculations are summarized in table 5. It is interesting to note that $[E(\text{SOEH}) + \Delta E_2]$ very closely reproduces $E(\text{Roothaan})$ for all the different values of $\theta(\text{H-C-O})$ studied by us. Also, except at $\theta(\text{H-C-O}) = 110^\circ$, $|E(\text{SOEH}) + \Delta E_2| < |E(\text{Roothaan})|$ for all other values of μ . Even for $\theta = 110^\circ$, $[E(\text{SOEH}) + \Delta E_2]$ only marginally shoots below $E(\text{Roothaan})$. For locating $\theta_{\text{min}}(\text{H-C-O})$ accurately, interpolation using cubic-splines was done with $E(\text{SOEH})$, $E(\text{Roothaan})$ and $[E(\text{SOEH}) + \Delta E_2]$ against θ . In all the cases θ_{min} turned out to be 133° (table 5). The final values of energy at θ_{min} estimated by the different methods have been given in table 5 for comparison. $[E(\text{SOEH}) + \Delta E_2]$ is found to be very close to $E(\text{Roothaan})$ at θ_{min} by lying slightly above the latter. $[E(\text{SOEH}) + \Delta E_2]$ can, therefore, be profitably utilised in geometry optimization as the estimation of ΔE_2 requires only a little effort. In fact, the total time required to compute the SOEH energy and the leading correction (ΔE_2) to it is approximately half the time required to calculate $E(\text{Roothaan})$ on the average. Further applications of this model for the calculation of equilibrium geometrical parameters of radicals are in progress and will be reported shortly. We would like to mention further that the method has been found to be applicable for the

Table 4. The observed μ -dependence of $E(\text{SOEH})$ and $[E(\text{SOEH}) + \Delta E_2]$ in HCO radical ($r_{\text{CH}} = 1.08$ Å, $\text{H-C-O} = 120^\circ$, $r_{\text{CO}} = 1.198$ Å)*

μ -values used	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
0.00	-25.87490	-25.87546	
0.40	-25.87810	-25.87848	
0.45	-25.87819	-25.87860	
0.50	-25.87824	-25.87869	-25.87942
0.55	-25.87826	-25.87877	
0.60	-25.87815	-25.87869	
0.65	-25.87802	-25.87863	
0.70	-25.87785	-25.87854	

* Bond lengths and angles from Sutton (1958).

Table 5. Variations in $E(\text{SOEH})$, $[E(\text{SOEH}) + \Delta E_2]$ and $E(\text{Roothaan})$ with changes in H-C-O angle of the HCO radical ($r_{\text{CH}} = 1.08 \text{ \AA}$, $r_{\text{CO}} = 1.198 \text{ \AA}$).

$\theta(\text{H-C-O})$ (degrees)	$E(\text{SOEH})$ (a.u.)	$[E(\text{SOEH}) + \Delta E_2]$ (a.u.)	$E(\text{Roothaan})$ (a.u.)
105	-25.86308	-25.86402	-25.86544
110	-25.86995	-25.87116	-25.87109
115	-25.87437	-25.87495	-25.87580
120	-25.87824	-25.87873	-25.87942
125	-25.88109	-25.88163	-25.88189
130	-25.88238	-25.88284	-25.88315
133	-25.88259	-25.88302	-25.88334
135	-25.88248	-25.88290	-25.88323
140	-25.88121	-25.88157	-25.88219
145	-25.87911	-25.87947	-25.88012
150	-25.87613	-25.87649	-25.87718

calculation of geometrical features of molecules in excited states (doublets and triplets). These results will be published in due course (Das and Bhattacharyya 1986).

5. Conclusions

The study reported in this paper has revealed a rather complicated analytical structure of the scaling parameter μ occurring in the SOEH model. The approximations used by us could only partially recover the optimum magnitude of the scaling parameter in different cases indicating the requirement for invoking a still higher order approximation for complete interpretation of the scaling parameter. However, the first or the leading correction (ΔE_2) to the SOEH energy has been found to be generally sufficient to reproduce $E(\text{Roothaan})$ very closely. The computational labour and cost is far less than is required for the calculation of $E(\text{Roothaan})$. Further generalization of the model appears to be necessary for a more complete understanding of the nature of the scaling parameter in the SOEH model.

Acknowledgements

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Magnetic susceptibility studies of lead oxyhalide glasses containing transition metal oxides†

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Abstract. Magnetic susceptibility studies of lead oxyhalide glasses containing high concentrations of transition metal oxides such as MnO and Fe_2O_3 have been performed. While they exhibit predominantly antiferromagnetic interactions, the low temperature ($< 100\text{K}$) region is dominated by paramagnetic contributions. The behaviour in these glasses is found to be similar to that of covalent oxide glasses and is different from that of purely ionic sulphate glasses.

Keywords. Magnetic susceptibility; oxyhalide glasses; transition metal oxides.

1. Introduction

Lead oxyhalide glasses in the systems, PbO-PbF_2 and PbO-PbCl_2 can be prepared with high concentrations of transition metal (TM) ions such as Fe_2O_3 and MnO (Rao and Rao 1985a). We have earlier investigated these glasses containing TM ions by ESR and optical spectroscopies (Rao and Rao 1985a, 1985b). It was found that Fe^{3+} ions prefer non-substitutional 4-coordinated sites of their own whereas Mn^{2+} ions acquire a slightly distorted octahedral coordination of the type, $[\text{MnO}_2\text{X}_4]$, ($\text{X} = \text{F}, \text{Cl}$) similar to the sites of Pb^{2+} ions in these glasses (Rao and Rao 1984; Rao *et al* 1984a, 1984b). It was also found that part of the added Mn^{2+} ions gets oxidized to Mn^{3+} state during glass preparation. In glasses containing high concentrations of Fe_2O_3 or MnO , magnetic interaction between TM ions is dominantly dipolar. But even then we observed (Rao and Rao 1985a) that a significant fraction of Fe^{3+} and Mn^{2+} ions are present in magnetically isolated sites.

We therefore consider that a study of the temperature dependence of magnetic susceptibilities is in order, since it provides information about the nature of the interaction between the TM ions. Additionally the curie constants evaluated from susceptibility measurements give information about the valence state of the TM ions. Further, the influence of non-magnetic (lead oxyhalide) host glass in which the ionicity of bonding increases with halide concentration is also worth investigating, because in purely ionic sulphate glasses the interaction between TM ions was found to be weakly ferromagnetic (Rao and Sundar 1981), whereas in most (covalent) oxide glasses the interaction was found to be antiferromagnetic (Shinkel and Rathenau 1965; Simpson and Lucas 1971; Hasegawa 1971; Egami *et al* 1972, 1973; Wilson *et al* 1973; Friebele and Koon 1974; Burzo *et al* 1982).

† Communication No. 324 from the Solid State and Structural Chemistry Unit.

In this short communication we present the results of our magnetic susceptibility studies of lead oxyhalide glasses containing high concentrations of MnO and Fe₂O₃. Our results suggest that the nature of interaction in these glasses is dominantly antiferromagnetic. We have discussed the possible origin of this effect.

2. Experimental

PbO-PbF₂ and PbO-PbCl₂ glasses containing various quantities of Fe₂O₃ and MnO were prepared by the procedure reported earlier (Rao and Rao 1985a). In this method, melts of appropriate composition containing 5 to 10 mol % of Fe₂O₃ or MnO (added as MnC₂O₄ which decomposes to MnO) were quenched into thin disks between two steel plates. The glasses so prepared were found to be homogeneous and no phase separation was noticed.

Magnetic susceptibility of these glasses in the temperature region of 15–300 K was measured by the Faraday method using a Cahn RG vacuum recording electrobalance. Specially shaped pole pieces are used for generating a constant field gradient. The maximum field used was around 4000 G. Hg[Co(NCS)₄] was used as calibrant. A closed cycle helium cryostat (model cs 202) manufactured by Air Products Inc., USA, was used for low temperature measurements. The molar magnetic susceptibilities reported here are corrected for diamagnetic contributions of the constituent ions in the glasses.

3. Results and discussion

Temperature variation of the inverse molar magnetic susceptibility, χ_M^{-1} , for various glasses containing different concentrations of Fe₂O₃ is shown in figure 1. Similar χ_M^{-1} vs T plots for glasses with different concentrations of MnO are presented in figure 2.

The temperature variations of the inverse susceptibilities exhibit the following interesting features: (1) There appears to be two linear temperature regions, one below 100 K (low temperature, LT region) and the other above 100 K (high temperature, HT region) in all glasses though this is only weakly apparent in MnO-containing glasses; (2) the susceptibility increases by almost an order of magnitude for a two-fold increase of Fe₂O₃ concentration while the increase is almost proportional to the concentration in the case of MnO; (3) the susceptibility increases enormously for heat treated glasses containing 0.5 mol % of Fe₂O₃. When the glass was heated above its crystallization temperature (≈ 600 K) for 2 hours; (4) the LT and HT regions in MnO doped glasses possess considerably smaller differences in slopes as compared to Fe₂O₃-doped glasses, in fact, Fe₂O₃-doped glasses exhibit distinctly large curvature in the region of 100 K, (5) the slope of the HT region of glass containing a higher concentration of MnO is lower than the corresponding slope in the glass containing lower concentration.

The two linear regions were visually identified and were least square fitted. The temperature variation of χ_M^{-1} in the two regions may be described by the Curie-Weiss law,

$$\chi_M = C/(T + \theta_p) \quad (1)$$

where C is the Curie constant and θ_p is an effective Curie temperature. Effective

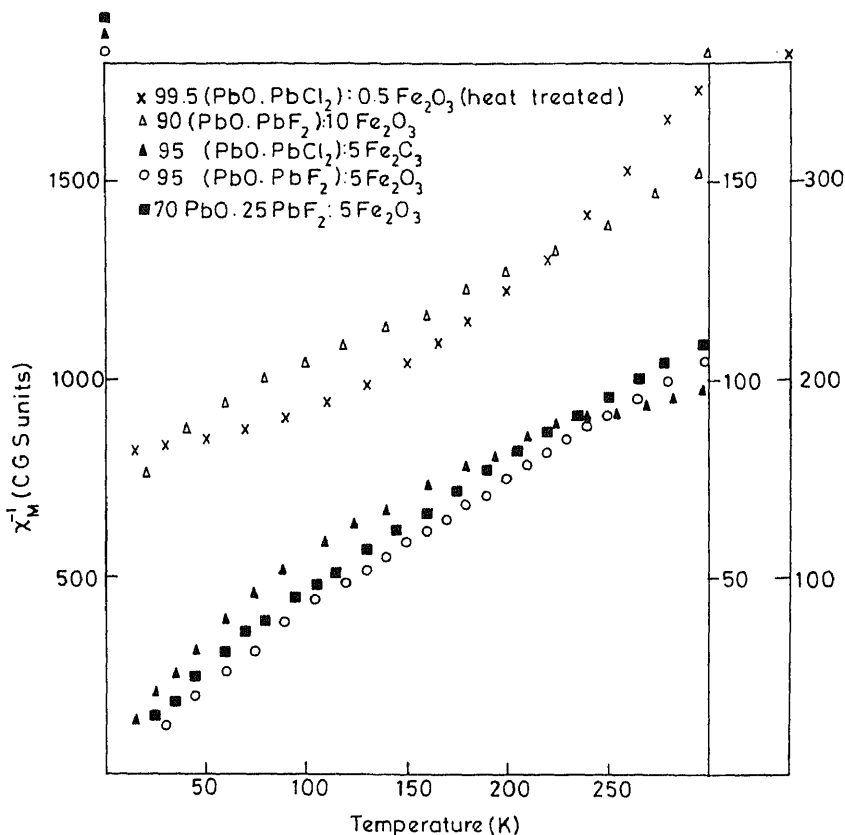


Figure 1. Temperature variation of inverse magnetic susceptibility for various glasses containing Fe_2O_3 . The y-axes for different curves in the figure are identified by the symbols at the top.

magnetic moment, μ_{eff} can be calculated from χ_M by the following formula

$$\mu_{\text{eff}} = 2.83 (C/x)^{1/2} \quad (2)$$

where x is the mole fraction of the transition metal ions in the glass. The calculated values of θ_p and μ_{eff} are given in table 1. The values of θ_p for the high temperature regions in all cases suggest that interactions are predominantly antiferromagnetic in these glasses. It may also be noted that glasses containing Fe_2O_3 give rise to larger θ_p values as compared to glasses containing MnO . Further, θ_p is higher for glasses with higher concentration of TM ions in the case of Fe_2O_3 whereas it is lower in the case of MnO . The magnitudes of θ_p suggest that the manganese ions are weakly coupled in the glass matrices in comparison to Fe^{3+} ions which are quite strongly coupled. This is quite in keeping with the structural features of these glasses in that the substitutional octahedral positions taken up by $\text{Mn}^{2+}/\text{Mn}^{3+}$ ions are spatially separated by larger distances than the tetrahedral positions preferred by Fe^{3+} ions. The spatial closeness of Fe^{3+} positions in these glasses is likely to be due to the tendency of Fe^{3+} ions to cluster

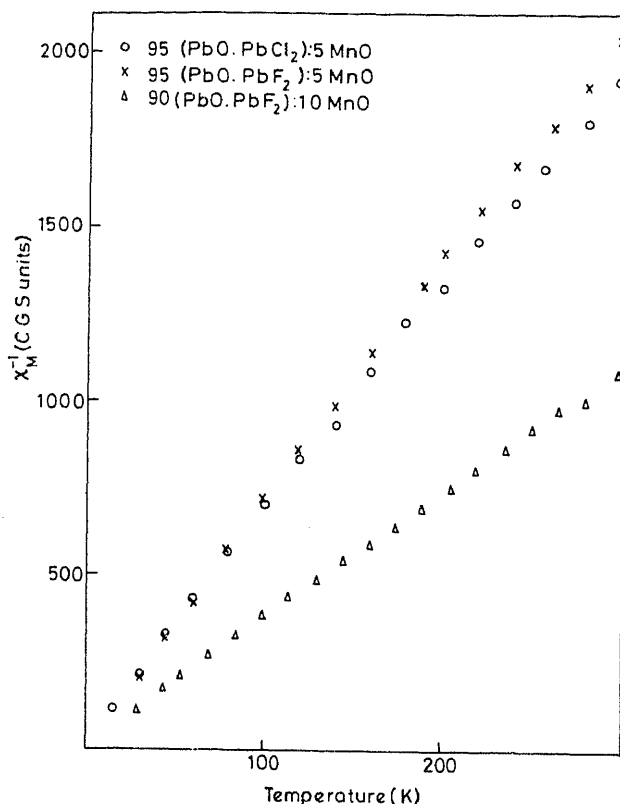


Figure 2. Temperature variation of inverse susceptibilities of various glasses containing MnO.

Table 1. Values of θ_p and μ_{eff} obtained from the high temperature (HT) region and θ_p values obtained from the low temperature (LT) region.

No.	Glass composition	LT region	HT region	
		θ_p	θ_p	μ_{eff}
1.	47.5 PbO:47.5 PbCl ₂ :5MnO	1.9	4.6	4.93
2.	47.5 PbO:47.5 PbF ₂ :5MnO	1.9	9.3	4.92
3.	45.0 PbO:45.0 PbF ₂ :10MnO	0.9	5.9	4.72
4.	47.5 PbO:47.5 PbCl ₂ :5Fe ₂ O ₃	12.0	116.4	7.84
5.	47.5 PbO:47.5 PbF ₂ :5Fe ₂ O ₃	2.6	35.0	5.04
6.	70 PbO:25 PbF ₂ :5Fe ₂ O ₃	9.5	45.3	4.99
7.	45.0 PbO:45.0 PbF ₂ :10Fe ₂ O ₃	—	132.3	13.83

crystallized by annealing at ≈ 600 K. The clustered Fe^{3+} ions behave ferromagnetically with high χ_M values (figure 1).

In the LT region (15–100 K) we observe that χ_M increases with temperature, which is

all cases, and is particularly large for Fe_2O_3 -containing glasses. This is reflected in decreased θ_p values. Such behaviour for an amorphous antiferromagnet was predicted by Simpson (1970) in his effective field model. This model assumes the presence of isolated magnetic ions in addition to those which interact with their magnetic neighbours. As the isolated ions do not interact with their neighbours (which are structurally far away) they contribute a small paramagnetic component to the total susceptibility which obeys the Curie law. This explains the susceptibility behaviour of these glasses in the LT region. The existence of isolated ions is a natural concomitant of the glassy state. A fraction of Mn^{2+} and Fe^{3+} ions are indeed present always in magnetically isolated sites even in glasses containing high concentrations of transition metal ions (as evidenced by characteristic low field ESR resonances) (Rao and Rao 1985a). Hence the LT region is dominated by paramagnetic interactions in almost all compositions. However, the nature of the interaction can be slightly different. In the glass containing 10 mol % MnO , the concentration of Mn^{3+} ions can be considerable (see later). This leads to Mn^{2+} - Mn^{3+} interactions which can result at the least in ferromagnetic interactions. This necessarily brings down θ_p even for the HT region. As it was noted earlier (table 1) θ_p is lower for glass containing 10 mol % MnO as compared to glass containing 5 mol % MnO .

In the case of $\text{PbO} \cdot \text{PbCl}_2$ glass containing 5 mol % Fe_2O_3 , another essentially linear HT region with a different slope above 225 K was observed (figure 1). This may possibly arise from strongly antiferromagnetically coupled near-neighbour Fe^{3+} ions present in the glass.

It may be noted from table 1 that μ_{eff} values for glasses containing 5 mol % MnO obtained from the analysis of the HT region are much lower than the free ion μ_{eff} value for Mn^{2+} ($5.92 \mu_B$) and are closer to that of Mn^{3+} ($4.90 \mu_B$). This value is even lower for the glass containing 10 mol % MnO , which suggests that the fraction of Mn^{3+} ions increases with added manganese concentration. These observations are quite in agreement with the results of our ESR and earlier optical spectroscopy studies. The μ_{eff} values for glasses containing 5 mol % Fe_2O_3 show that most of the ions are present as Fe^{3+} . However, it is not likely that Fe^{2+} ions are also produced during equilibration at melting temperature like in other lead oxide containing glasses (Burzo *et al* 1980). Nevertheless, Fe^{2+} ions may not aggregate into regions dominated by Fe^{3+} ions. Hence Fe^{2+} ions, if any, make contributions only to paramagnetic susceptibility and not to ferromagnetic type as expected in manganese containing glasses. The μ_{eff} value for the glass containing 10 mol % Fe_2O_3 is very high ($13.83 \mu_B$) and may be due to the onset of dominant ferromagnetic interactions in isolated clusters.

The results discussed above point to the fact that magnetic interactions in lead oxyhalide glasses containing transition metal ions are essentially antiferromagnetic as in other covalent oxide glasses and they are different from the type of interactions in purely ionic sulphate glasses. In fact the θ_p value for a PbO -rich glass ($70\text{PbO} \cdot 25\text{PbF}_2 \cdot 5\text{Fe}_2\text{O}_3$) is higher than that of PbO -poor ($47.5\text{PbO} \cdot 47.5\text{PbF}_2 \cdot 5\text{Fe}_2\text{O}_3$) glass in the case of glasses containing 5 mol % Fe_2O_3 (glass nos. 5 and 6 in table 1). Since the magnetic interactions are most likely mediated by oxygen atoms in a super-exchange type of interaction we feel that the covalency of oxygen bonding dictates an antiferromagnetic spin orientation in these glasses. We have also noted elsewhere (Rao *et al* 1984a) that in PbO - PbF_2 glasses fluorine tends to occupy network positions with an apparently covalent Pb-F interaction. This is also likely to play a role in the covalency effect on magnetic interactions in these glasses.

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Foreword

The Solid State and Structural Chemistry Unit of the Indian Institute of Science organized a Winter Workshop on Solid State Chemistry during 9–16 December 1985. The Workshop was sponsored by the University Grants Commission, New Delhi and the Department of Science and Technology, Government of India, under its IRHPA Programme.

The purpose of the Workshop was to focus attention on current trends in various aspects of solid state chemistry and to acquaint teachers and research workers in universities with recent developments in this area. The important topics covered were structural chemistry of oxides, computer simulation study of zeolite catalysts, structure and properties of glasses, Verwey transition in Fe_3O_4 , superconductivity in ternary compounds, solid surfaces, low dimensional solids, electron-electron interaction in one-dimensional solids, fast ion transport in solids, dynamics of crystal growth, reactivity of solids, heavy fermions, quasicrystals and metal-insulator transitions.

The programme of the Workshop comprised 40 invited talks and special lectures, giving ample time for discussion. There were seven lecturers from abroad and several from within the country. The total number of participants was around 40; in addition, a large number of students and faculty members of the Indian Institute of Science participated.

This issue of the Proceedings is devoted to articles dealing with some of the topics discussed at the Workshop. Some of the topics that were presented in the Workshop but not covered in this issue are quasicrystals, heavy fermions, superconductivity in ternary compounds and amorphous materials. We hope that the articles published in this issue will be of interest not only to solid state chemists engaged in research and teaching, but also to those working in condensed matter in general.

J. Gopalakrishnan
Coordinator of the Workshop
on Solid State Chemistry

C. N. R. Rao
Editor of Publications,
Indian Academy of Sciences.

The synthesis, crystal growth, and characterization of nonstoichiometric magnetite

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Abstract. A review is provided concerning the thermodynamic and electrical characteristics of nonstoichiometric magnetite, $\text{Fe}_{3(1-\delta)}\text{O}_4$. Great stress is placed on the need for careful preparation and appropriate annealing of single crystal specimens. Information needed to prepare material of a given δ value is provided. For $\delta \leq 0.0039$ magnetite undergoes a first-order phase change at the Verwey transition; for $\delta > 0.0039$ the change is of second or higher order. Corresponding types of changes are encountered in resistivity and Seebeck coefficient measurements. Some aspects of the Verwey transition are discussed.

Keywords. Magnetite; metal-insulator transitions; heat capacity measurements; electrical properties.

Historical commentary

Magnetite has been recognized as an important substance since antiquity; Plinius and Dioskorides were among the early natural philosophers interested in the properties of this material which is referred to under the generic name of lodestone. It was the magnetic properties of this class of minerals that held the interest of many natural philosophers for centuries. More systematic investigations were initiated by Gay-Lussac (1811, 1812), Dalton (1816), and Berzelius (1826). The fundamental physical properties of this material were more firmly established by numerous investigators in the period 1850–1925. In particular, the scientific analysis of the ferrimagnetic properties of magnetite was placed on a sound footing only after the fundamental analysis of this phenomenon by Néel (1948).

The first report of an anomaly in Fe_3O_4 occurring in the range 113–117 K seems to have been published in 1926 by Parks and Kelley (1926), on the basis of specific heat measurements. This was followed by further exploratory investigations by Okamura (1932) of several other properties, all of which exhibited anomalies in the 100–125 K range. Verwey (1939) published a seminal article in which he directed attention to a discontinuity in electrical resistivity near 120 K as a manifestation of a transition that now bears his name. Already in this first paper the nature and temperature of the transformation was shown to be sensitive to small changes in the oxygen/iron ratio in Fe_3O_4 , but his recognition of the need to control sample compositions was not properly followed up in most of the work published on the subject since that time. As a consequence, there is considerable diversity in the reported experimental results; this, in turn, has produced many different theories designed to elucidate the nature of the Verwey transition. It has only recently been properly appreciated that the phenomenon is intimately linked to the mixed valence properties of the cation, i.e., to the ratio of iron

value, by changes in the O/Fe ratio or by the presence of impurities. This, in turn, calls for precise control over sample preparation techniques. Since sufficient care with respect to these matters has not always been exercised in the past, a renewed study of even the most fundamental properties with adequately prepared specimens has become extremely important. One such data have been put on a firm footing the number of viable theoretical models describing the transition will also be greatly reduced.

In light of the above, we first discuss methods of sample preparation and characterization that lead to specimens of adequate perfection. We then describe a series of recent studies which shed new light on the phenomenology of the Verwey transition. Lastly, we comment briefly on some implications of these findings. For earlier reviews of the status of the field the reader is referred to articles by Mott (1979, 1980) and by Honig (1982).

Preparation of specimens

Fe_3O_4 or Fe_2O_3 is available commercially in powdered form with low levels of impurities. The first task facing the investigator is the growth of single crystals by a technique which avoids sample contamination. A very effective method by which sizeable crystals may be grown is the skull-melting operation shown schematically in figure 1a (Harrison and Aragón 1978; Harrison *et al* 1983). The output of a 50 kw rf generator operating at 3 MHz is routed to a coil wound around a copper crucible, depicted in figure 1b. The vertical fingers and sections of the split base are individually water-cooled and spaced sufficiently far apart to permit penetration of the electromagnetic field into the sample space; eddy currents through the metal container are also minimized by this arrangement.

As for any metal oxide, it is essential to control the oxygen fugacity above the specimens to ensure that the correct phase is obtained. One method for achieving this objective, both during crystal growth and in subsequent annealing processes, is to expose the sample to a CO/CO_2 gas mixture which is circulated above the specimen. At any particular temperature the equilibrium between these components establishes a definite oxygen fugacity through the reaction



The oxygen fugacity, f_{O_2} , is given by

$$K = (f_{\text{CO}}/f_{\text{CO}_2})f_{\text{O}_2}^{1/2}, \quad (2)$$

where the equilibrium constant K is fixed at any specified temperature; the ratio $f_{\text{CO}}/f_{\text{CO}_2}$ is adjusted experimentally through control of the relative rates of flow of these two gases into the chamber. At a given temperature the oxygen fugacity is then uniquely specified. One should note that according to figure 2, at volume flows for which the percentage of O_2 in the gas mixture ranges from 100 to 94.3%, one remains inside the stability limits of the magnetite phase; the various oxygen fugacity curves change with temperature in a manner approximately parallelling the change of the f_{O_2} curves corresponding to the phase boundaries.

During crystal growth one encounters the problem that Fe_3O_4 melts incongruently; because of their different $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios, liquid and solid magnetite at the melting point require different oxygen partial pressures for equilibration. It was found

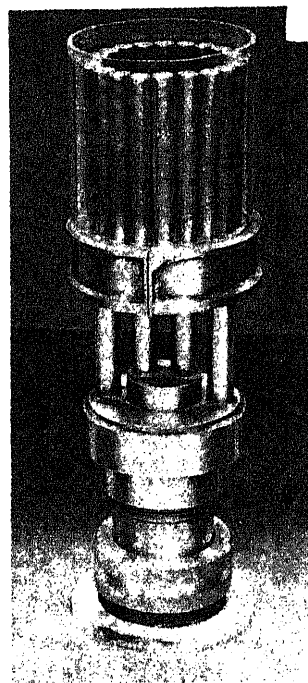
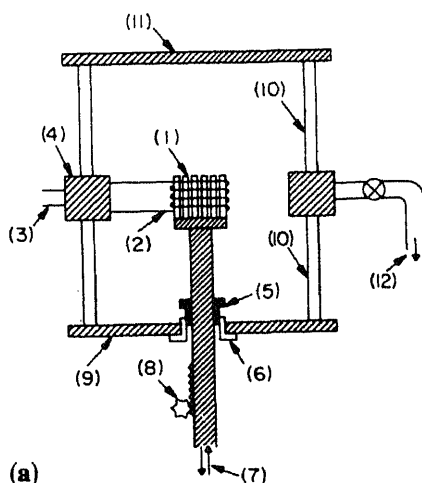


Figure 1(a). Schematic diagram of skull melter. (b). Photograph of a water-cooled copper container for use with skull melter.

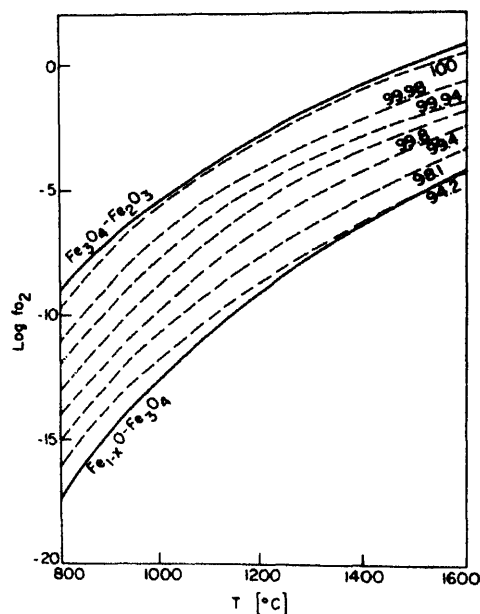


Figure 2. Phase stability diagram for magnetite. The solid boundaries depict the oxygen fugacities required at the magnetite-wüstite and magnetite-hematite phase boundaries. The dashed lines show oxygen fugacities achieved with several CO_2/CO mixtures; figures quoted pertain to the $\text{CO}_2/[\text{CO} + \text{CO}_2]$ content of the circulating gases.

empirically that boules containing single crystals could be grown by use of 100% CO₂ as the circulating gas; however, the materials so obtained tend to be cation deficient and nonuniform in composition. This difficulty can be remedied by subsequent subsolidus annealing as described later; in the course of this process the proportions of CO and CO₂ have to be fixed at prescribed values discussed below.

The melting process itself is initiated by placing a graphite ring on top of the Fe₃O₄ charge; the ring readily couples to the rf power supplied through the coils and thus heats contiguous regions of the powder sufficiently so that these, in turn, couple to the electric power. An avalanching process ensues until all the material becomes molten except for a layer of sintered material adjacent to all water-cooled surfaces of the copper container. This thin skull forms the 'crucible' for the molten Fe₃O₄ mass; the graphite susceptor burns off in the mildly oxidizing atmosphere above the sample. There is provision to add more powder by use of a hopper on top of the unit shown in figure 1a. A rack and pinion device lowers the molten mass through the coil to a cooler zone, thus allowing all the material to freeze slowly, and to form a solid boule. The latter then is opened up; single crystal magnetite ranging from less than 0.5 g to more than 20 g (and to 70 g on one occasion) may then be removed from the centre.

Annealing of specimens

While crystals prepared as described above appear to be of high quality to the unaided eye they are generally quite nonuniform in their O/Fe ratio even within the same single crystal because of the incongruent melting problem described earlier and because of the severe thermal gradients that exist in the cooling process.

To circumvent the difficulty the single crystal nuggets are oriented and sliced to obtain samples of desired dimensions. Specimens so produced are then annealed at temperatures below their melting point. The annealing requirements involve two determinations: the appropriate oxygen fugacity to which the sample is to be subjected during the reheating process, and the length of time required to achieve uniformity of composition during that particular subsolidus anneal.

The oxygen fugacity is set by the desired degree of deviation δ from ideal magnetite stoichiometry to achieve the specified composition Fe_{3(1- δ)}O₄. The appropriate thermodynamic analysis (Aragón *et al* 1982) is based on the following two equations (Flood and Hill 1957) that govern the equilibration processes of magnetite with oxygen gas:



and



Here V is a vacancy in the cation sublattice and I is an interstitialcy arising from the formation of Frenkel defect pairs. These two entities can recombine to yield a normal cation

$$V + I = 0. \quad (5)$$

following relation between the oxygen fugacity f_{O_2} and δ :

$$f_{\text{O}_2}^{1/4} = \frac{1}{K_2} \left\{ 2 + \frac{24\delta}{1 - 8\delta - \frac{\delta}{2} - \frac{1}{2}[\delta^2 + 4K_1]^{1/2}} \right\} \left\{ \frac{\delta}{2} + \frac{1}{2}(\delta^2 + 4K_1)^{1/2} \right\}^{3/8}, \quad (6)$$

wherein

$$K_1 = n_v n_i / n_\Sigma^2, \quad (7)$$

is the equilibrium constant for the formation of Frenkel defect pairs, and

$$K_2 = \frac{n_{\text{Fe}^{3+}}}{n_{\text{Fe}^{2+}}} f_{\text{O}_2}^{-1/4} \left(\frac{n_v}{n_\Sigma} \right)^{3/8}. \quad (8)$$

In the above n_v , n_i , n_Σ are the mole numbers of cation vacancies, of cations located interstitially, and of total cations, respectively. The equilibrium constants K_1 and K_2 can be evaluated from the carefully executed set of thermogravimetric experiments (Dieckmann 1982) by the determination of δ as a function of f_{O_2} at several temperatures while the sample remained equilibrated with the ambient. It was found that

$$\log K_2 = \frac{4456}{T} - 2.64, \quad (9)$$

$$\log K_1 = \frac{-10740}{T} - 1.23. \quad (10)$$

The dependence of $\log f_{\text{O}_2}$ on $10^3/T$ is shown in figure 3 for several selected δ values within the magnetite-hematite and magnetite-wüstite phase boundaries shown on the diagram. One should note in particular that the stability curves corresponding to $\delta > 0$ and $\delta < 0$ are concave and convex respectively; thus, they ultimately cross the boundary lines delineating the phase stability limits for magnetite. Therefore, if one gradually cools a specimen enclosed in a container, so as to maintain the system isostoichiometric (i.e. at a fixed composition), one runs the risk of ending up with a two-phase mixture

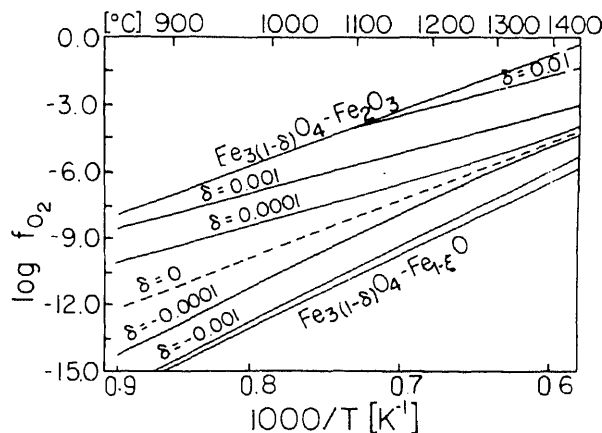


Figure 3. Intrinsic oxygen fugacity for single crystalline $\text{Fe}_3(1-\delta)\text{O}_4$ and stability field

unless the process is kinetically hindered; this problem may usually be avoided by a rapid quench. It is, however, necessary to check samples for the absence of extraneous phases (see below) after any cooling process even when the latter is carried out with a totally encapsulated magnetite sample.

In figure 4 is shown the variation of δ versus $\log f_{\text{O}_2}$ at 1400°C as calculated from (6)–(10); the curves for the range 1300°C to 900°C are similar in appearance but the maximum excursions from $\delta = 0$ become considerably smaller, as is also evident from inspection of figure 3. One thus has available all the information required for the preparation of magnetite samples of a specific stoichiometry within the limitations imposed by the requirements of maintaining single-phase samples.

There then remains the question of the length of the anneal time needed to ensure a uniformity of composition within the bulk of the sample. This matter is addressed by examination of the diffusion rates of the cations in response to the addition or subtraction of oxygen in the lattice during equilibration. The requisite information is contained in figure 5 which represents a concentration profile for the motion of vacancies through a semiinfinite slab. The parameter associated with each curve is specified by Dt/l^2 , where l is the half-thickness of the slab, t is the time, and $D \approx D_{\text{Fe}}^*/[V]$ is the vacancy diffusion constant, related as shown to the Fe tracer diffusion constant D_{Fe}^* and to the cation vacancy concentration $[V]$. The requisite D_{Fe}^* values are available from a study of Dieckmann and Schmalzried (1977); based on these results, typical times required for sample homogenization are shown as part in the figure caption. At first glance it appears highly desirable to operate at 1400°C so as to minimize the time for achieving a uniform sample composition. However, this then also requires an extremely fast quench so as not to disturb the uniformity of composition during the cooling process. Thus, it is easier to operate at 1000°C where the quenching process does not present a problem. On the other hand, as already mentioned, the maximum value of δ increases with rising temperatures; thus, to reach the larger values of δ it is necessary to carry out anneals at 1400°C. As is seen from the figure, homogenization of a slab is complete in a time scale of minutes for samples whose thickness is in the mm range. This means that, even for very fast quenches, the surface layers change in composition as the sample cools. An appropriate operating procedure

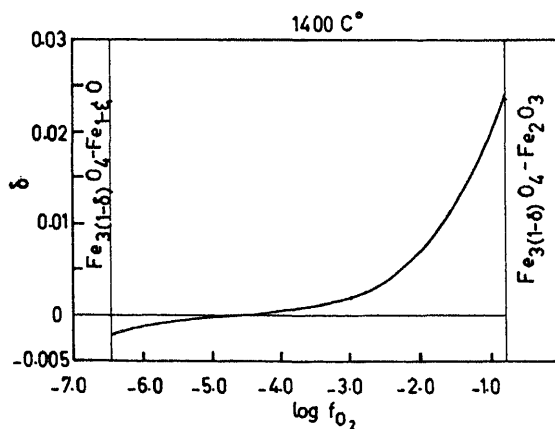


Figure 4. Variation of parameter δ with $\log f_{\text{O}_2}$ at 1400°C.

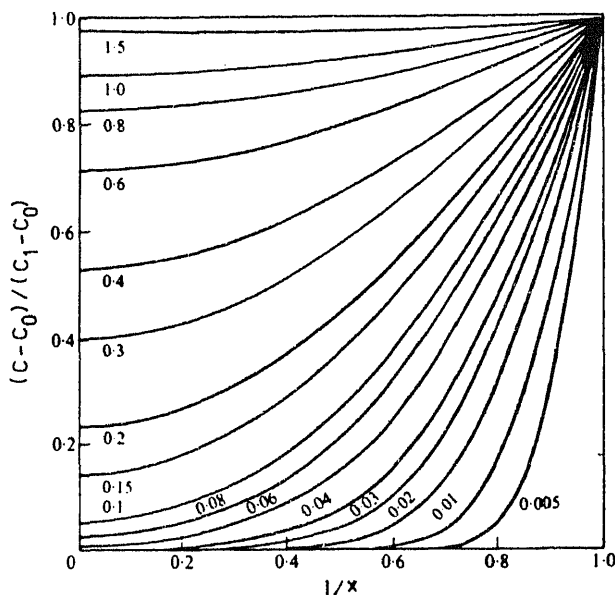


Figure 5. Concentration profiles for bulk diffusion. C represents the concentration of the diffusing species; C_1 is the surface concentration and C_0 , the uniform concentration; x is the distance along the concentration gradient and $2l$ is the thickness of the sheet. The numerical labels for the graphs represent values of Dt/l^2 . The minimum time requirements for homogenization of slabs of 1 and 10 mm thickness at 1000°C are 3 hrs and 306 hrs and at 1400°C are 2 min and 14 hrs, respectively.

in such cases is to anneal larger specimens than actually needed for the measurements and to trim off the surface layers of the quenched samples to a depth such that the remaining core is uniform in composition.

During the anneal one must continually monitor the oxygen fugacity; this may conveniently be done by use of an electrochemical $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid electrolyte cell of a design described elsewhere (Shepherd and Sandberg 1984).

Additional checks of sample quality

Before specimens are finally used in measurements it is very desirable to carry out additional checks concerning sample quality. Among these are the following:

(i) A neutron activation analysis to monitor the impurity content of the samples. Any aliovalent cations or anions present alter the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the sample in competition with variations in oxygen stoichiometry. This effect is particularly deleterious in stoichiometric specimens ($\delta \rightarrow 0$), as is demonstrated in figure 6 discussed below.

(ii) Powder and Laue backscattering x-ray diffraction studies provide a check on the absence of gross inhomogeneities and show whether the specimens are indeed monocrystalline. One should note that the techniques are not suited for checking the

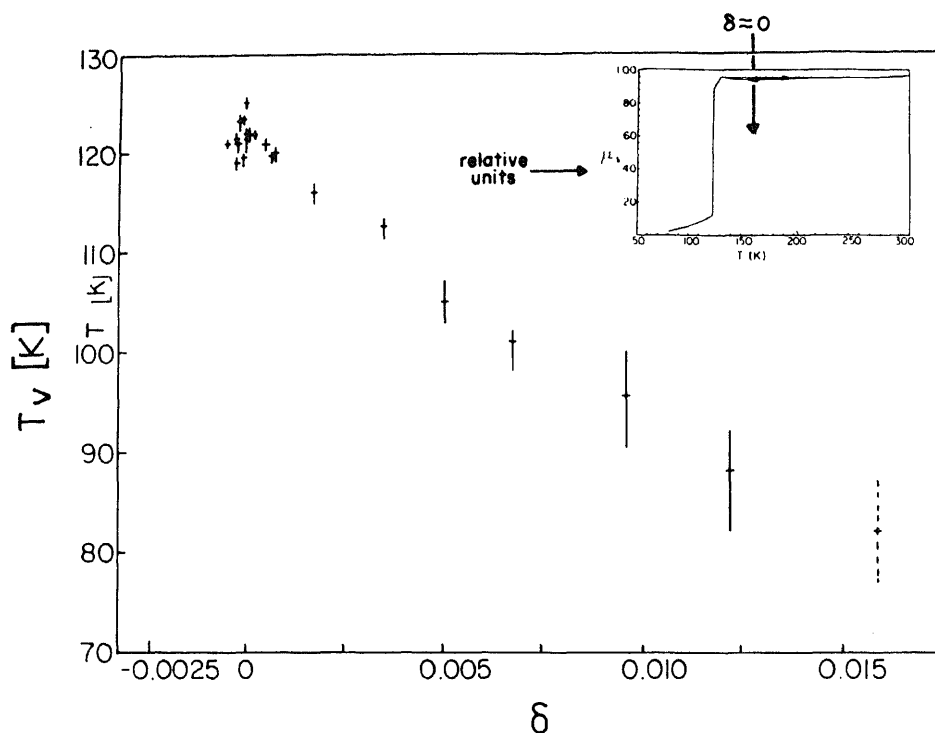


Figure 6. Variation of Verwey transition temperature with nonstoichiometry parameter. Measurements were carried out by thermomagnetic analysis, based on the measurements of initial permeability (see inset). Note the scatter of points near $\delta = 0$, and the difference in data for small ($\delta \leq 0.004$) and large ($\delta \geq 0.004$) deviations from ideal stoichiometry ($\delta = 0$).

(iii) Polarized light microscopy is very useful in routinely detecting microscopic aggregations of phases such as wüstite or hematite in the magnetite matrix, particularly at internal grain boundaries. The degree of perfection of crystal growth as manifested by the presence or absence of voids and other large-scale imperfections can also be monitored.

Experimental results: the Verwey transition temperature

We now summarize briefly under several headings some of the work carried out at Purdue University on high quality samples produced and monitored as shown above. The first set of measurements dealt with the determination of the Verwey transition temperature. A rapid and convenient means of accomplishing this task is to perform initial magnetic permeability studies (Aragón *et al* 1985). The technique relies on the drastic change in the cubic anisotropy energy at the Verwey transition (Chikazumi 1975) which is then manifested in a dramatic rise of the initial permeability as the temperature T is elevated past the transition temperature T_v ; a typical experimental curve is shown as the inset in figure 6. Results read off from such measurements are entered in the main portion of the figure; the vertical lines show the temperature range

near T_v over which there is a rapid change in initial permeability in response to the comparably large change in anisotropy energy. The dot near the centre of the vertical lines represents the inflection point in the rapidly ascending permeability and closely corresponds to the Verwey temperature. It will be noted that the vertical lines in figure 6 become larger beyond a certain δ value; the reason for this observation will be discussed shortly. The principal feature of these measurements is that the transition temperature T_v drops nearly linearly with rising δ from a high of $T_v \approx 125$ K at $\delta \approx 0$ to a low of $T_v \approx 81$ K near $\delta = 0.012$. The scatter of points near $\delta = 0$ arises from the presence of different amounts of impurities in the various specimens; only for $\delta > 0.0005$ do the effects associated with stoichiometric variations δ outweigh those of the impurities. This provides a graphic illustration of the need to work with very pure specimens if one wishes to measure properties intrinsic to nearly stoichiometric Fe_3O_4 .

One can now also understand why such a diversity of T_v values have been quoted in the literature. In many instances workers carried out measurements on unannealed specimens and hence, on samples of unknown composition. Also, for nonuniform specimens different parts of the material may undergo the transition at somewhat different temperatures, so that the transition may seem to be broadened out.

Heat capacity studies

The Verwey transition, as any phase change, must first be understood in terms of the changes in thermodynamic properties that occur in the neighbourhood of the transformation. Accordingly, a series of heat capacity measurements were undertaken on samples of different oxygen stoichiometry. The initial objective was to settle long-standing differences in reports concerning the nature of the heat capacity anomalies that accompany the Verwey transition. In most of the measurements published earlier the anomaly extended over some twenty kelvins; for a review of this work see Shepherd *et al* (1985). Also, multiple peaks were frequently observed which, in turn, prompted theories that interpreted the Verwey transition as occurring in successive stages. Finally, the persistence of short-range order to temperatures far above the Verwey transition has frequently been reported.

The measurements described below were carried out on a relaxation type calorimeter (Griffing and Shivashankar 1980) in which a pulse of heat is applied and the subsequent temperature relaxation is monitored. Under appropriate operating conditions the temperature changes exponentially with time. From the rate constant of the temperature reequilibration it is possible to determine the heat capacity C_p (Bachmann *et al* 1972). The advantage of this procedure is that one can carry out measurements with very small samples (20–60 mg in mass), so that time lag problems with large specimens are avoided. The equipment may also be operated in a transition mode procedure, whereby cooling or heating curves are taken; this permits the determination of heats of transition at $T = T_v$.

The results depicted in figure 7 are typical of those obtained for specimens in the composition range $-0.0002 < \delta < 0.004$. One encounters a single sharp spike in the heat capacity whose width, excepting the small shoulders on which the spike is superposed, does not exceed 0.4 K. A typical heating curve for specimens in this range is shown in figure 8. It is seen that for a considerable range of compositions the

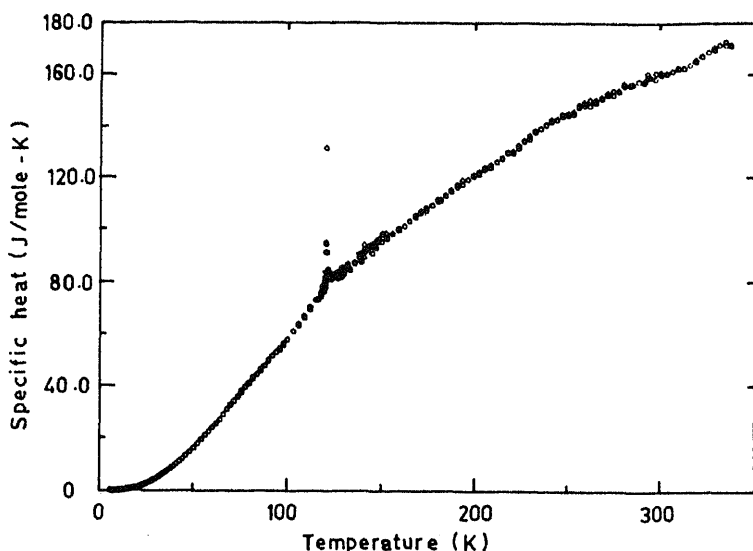


Figure 7. Heat capacity curve for a nearly stoichiometric magnetite single crystal. Note the sharp transition at the Verwey temperature.

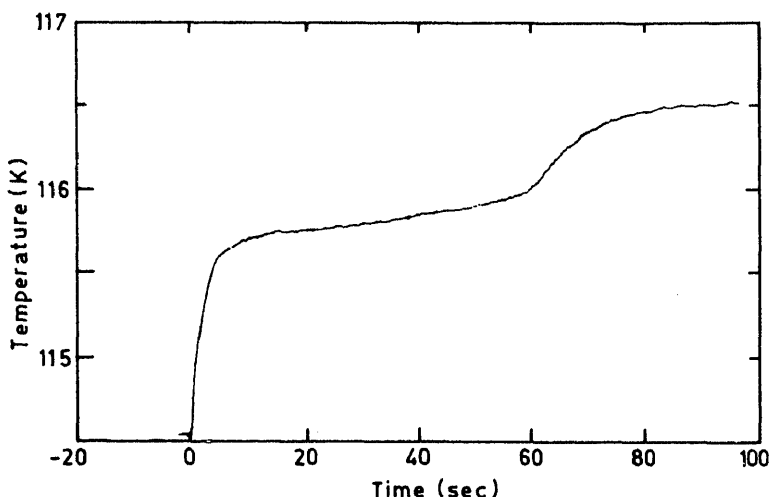


Figure 8. Heating curve for a nearly stoichiometric sample undergoing the Verwey transition. Note the temperature scale of the ordinate.

neighbourhood of $\Delta T = 0.2$ to 0.4 K, and this span diminishes as the total temperature range of the heating or cooling cycle is decreased. It appears that ΔT is actually determined by instrumental resolution problems, so that the quoted ΔT values represent upper limits.

In conformity with the results of figure 4, the transition temperature, as monitored

deal 4/3 O/Fe stoichiometry. The transition entropy as computed from the area under the heating or cooling curves is $\Delta S_v = R \ln 2$ mole Fe_3O_4 for specimens with $\delta \approx 0$. This is half of the anticipated value if the Verwey transition involved single ion species in a sudden transition from complete charge ordering to complete disordering. This matter is further discussed below.

One of the newly discovered features in the above investigation is that in the compositional range between $\delta = 0.0035$ and $\delta = 0.0049$ the transition suddenly switches to a second (or higher) order regime. This is documented first by the absence of any thermal arrests in the heating curves shown in figure 10; within the noise level these

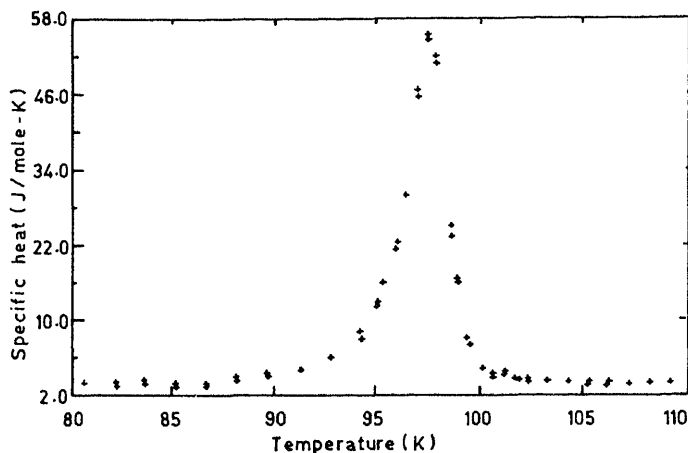


Figure 9. Excess heat capacity curve for a $\text{Fe}_{3(1-\delta)}\text{O}_4$ specimen with $\delta = 0.0068$. Background curve similar to that shown in figure 7.

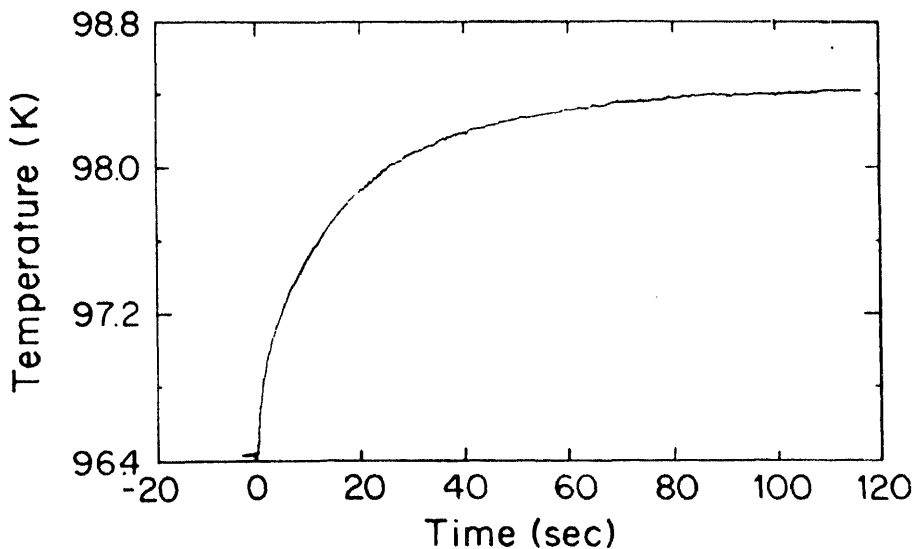
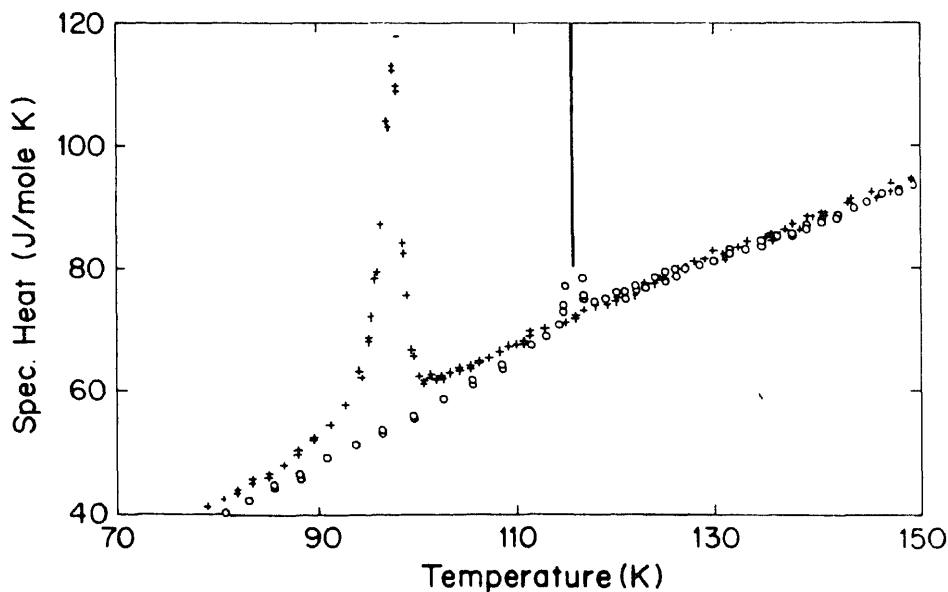


Figure 10. Thermal heating curve for sample whose heat capacity anomaly near the Verwey

vary strictly exponentially with time. Second, these samples exhibit a very broad, Λ -type heat capacity anomaly, as shown in figure 9, where the excess heat capacity is plotted after subtraction of the background. This broad anomaly is not simply a superposition of several first-order peaks such as might be brought about by inhomogeneities in sample composition. For, the background traces outside the temperature range of the anomalies for samples undergoing the first order transition (hereafter termed group A samples) lies below the corresponding traces for the samples undergoing the second order transition (termed group B samples). Also, the heating or cooling curves for group B samples at $T = T_v$ are strictly exponential. The new features are demonstrated in figure 11; such a state of affairs persists in the temperature range $T < T_v$ down to the lowest measured temperatures. For $T > T_v$ the two types of heat capacity curves merge (or nearly merge), irrespective of whether the sample executes a first- or second-order transition to reach the cubic spinel phase. The above is in accord with the thermodynamic approach to second- (or higher-) order transitions; in principle, such an anomaly sets in at zero temperature and the deviations from the background trace grow continually until the anomaly terminates abruptly at the transition temperature. By contrast, numerical calculations of the entropy S (J W Koenitzer, J P Shepherd and P Wang, unpublished research) have shown that the change of S with temperature T for group B samples differs considerably from $S(T)$ curves for group A samples, as is shown in figure 12. The fact that for $T > T_v$ the heat capacity curves of the various $\text{Fe}_{3(1-\delta)}\text{O}_4$ specimens essentially match while the entropy curves fail to do so, suggest that electronic degrees of freedom and charge ordering processes are the important contributing factors in the Verwey transition.

One should note that only by the use of properly prepared samples was it possible to detect the subdivision of the Verwey transition into first- and second-order types and to



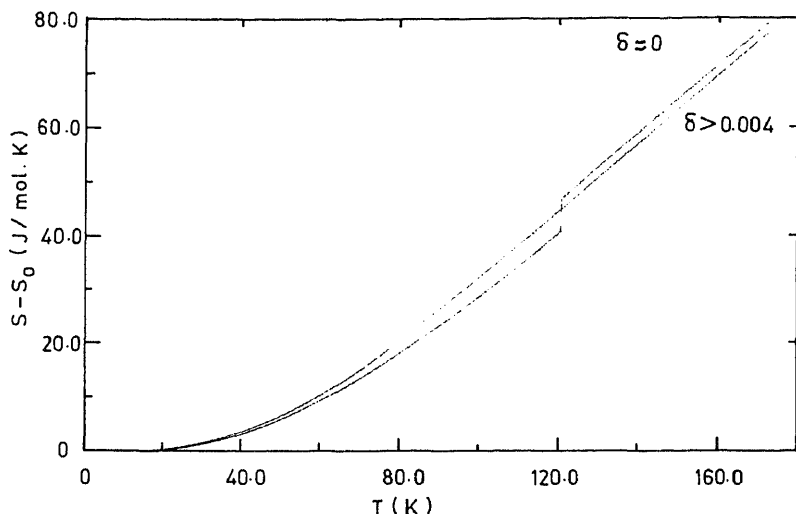


Figure 12. Entropy curves for group A ($\delta \approx 0$) and group B ($\delta = 0.0049$) specimen as determined from heat capacity data.

achieve the very sharp set of heat capacity anomalies for the former group. Apparently, in virtually all prior measurements samples of dubious provenance were employed, so that with specimens of nonuniform composition the thermodynamic properties of magnetite could not be correctly discerned. One of the few exceptions was the research by Gmelin *et al* (1983) who were apparently the first to show that narrow transition ranges could be achieved in calorimetric studies and that changes in T_v were encountered by annealing either single crystals or polycrystalline aggregates under different oxygen fugacities.

The mechanism by which Fe_3O_4 undergoes either the first or the second order transition is still undetermined. However, two quite general inferences may be drawn. The first is that the entropy change at the first-order Verwey transition is not consistent with a randomized mixing of Fe^{2+} and Fe^{3+} ions out of some elementary, ordered configuration. As stated earlier, the latter process would lead to a value $\Delta S_v = 2R \ln 2/\text{mole Fe}_3\text{O}_4$ when $\delta = 0$. Rather, the observed values, $\Delta S_v = R \ln 2/\text{mole Fe}_3\text{O}_4$, may be rationalized in terms of the formation below T_v of $\text{Fe}^{2+}\text{--Fe}^{2+}$ and $\text{Fe}^{3+}\text{--Fe}^{3+}$ dimer units in chains along the $\langle 110 \rangle$ directions of the octahedral planes. This structure is one of several types proposed by Kita *et al* (1983) as being consistent with nuclear magnetic resonance and Mössbauer data. Such consistency naturally does not constitute a proof for the correctness of such an arrangement, but it does appear to rule out charge ordering at the level of single ions.

The second concerns the value of the critical δ_{cr} at which the system switches from the first to the second order transition. The low-temperature monoclinic unit cell of dimension $\sqrt{2}a \times \sqrt{2}a \times 2a$ (where a is the lattice parameter of the spinel) contains 32 formula units of Fe_3O_4 , i.e. $n_{\Sigma} = 96$ cations. In the course of increasing the O/Fe ratio

earlier, the density of vacancies V and interstitials I are related by $n_V n_I / n_\Sigma = K_1$ where K_1 is the equilibrium constant. Let us concentrate on the first of the above equations, (1): When the oxidation step has reached the stage such that one cation per unit cell has been converted from the 2+ to the 3+ configuration, (3/8) of a vacancy has also been generated. The fractional change in oxygen/cation stoichiometry at that point is therefore $\delta_{cr} = (3/8)/96 = 0.0039$, which falls comfortably in the range $0.0035 < \delta < 0.0049$ where the changeover in transition is observed to occur.

Lastly, it is important to note that there is no indication in these thermodynamic measurements either of an extra anomalous C_p peak at 10 K or of the persistence of short-range order (SRO) above T_v , which type of ordering has frequently been postulated. Careful examination of all heat capacity data in our measurements confirmed the findings of Yumoto *et al* (1984) who specifically searched for but failed to detect any heat anomalies in the cryogenic temperature range. Also, we do not encounter any offset in the C_p baselines above T_v as compared to below T_v . Thus, our thermodynamic measurements by themselves do not substantiate the existence of SRO effects.

Resistivity measurements

The question naturally arises whether the two types of thermodynamic transitions have their counterpart in electrical properties. To settle this matter it is especially important to carry out resistivity studies on appropriately grown single crystal specimens. The dangers inherent in doing such measurements on polycrystalline specimens are too well known to require elaboration here. Indeed, while the results cited below do qualitatively resemble resistivity data obtained on sintered ceramics there are significant differences on a quantitative level, and these are important when one inquires into the mechanism of charge transport in magnetite.

The change of resistivity ρ with temperature T is shown in figure 13 for a variety of $\text{Fe}_{3(1-\delta)}\text{O}_4$ single crystals prepared as discussed earlier (Aragón *et al* 1985b). This set appears to be the first truly systematic investigation of its type. Careful inspection reveals several interesting features: (i) One can clearly distinguish between group A and group B samples: the former undergo a discontinuous change in ρ at $T = T_v$; for the latter there is an anomalous rise in ρ at $T = T_v$ but no discontinuity. Hysteresis effects are clearly in evidence for samples in group B. The origin of this phenomenon is unclear at this point, because one does not ordinarily associate hysteretic effects with second order transitions. (ii) In conformity with observations cited earlier, the Verwey transition temperature diminishes monotonically with rising δ . (iii) The size of the resistivity discontinuity or anomaly diminishes with increasing δ . (iv) The resistivity curves above T_v essentially coincide for all samples, whereas there is a considerable, systematic spread in the curves for $T < T_v$, brought about by the effect mentioned in (iii); the largest resistivities are encountered for samples with $\delta \leq 0$. (v) Finally, it should be mentioned that these measurements have elements in common with earlier, less complete investigations on single crystals by Kuipers and Brabers (1976, 1979) and by several earlier investigators (Miles *et al* 1957; Siemon 1970; Chikazumi 1975; Terukov *et al* 1979). All of these latter measurements were carried on specimens sufficiently close to stoichiometry to yield discontinuities in ρ at the transition point, but

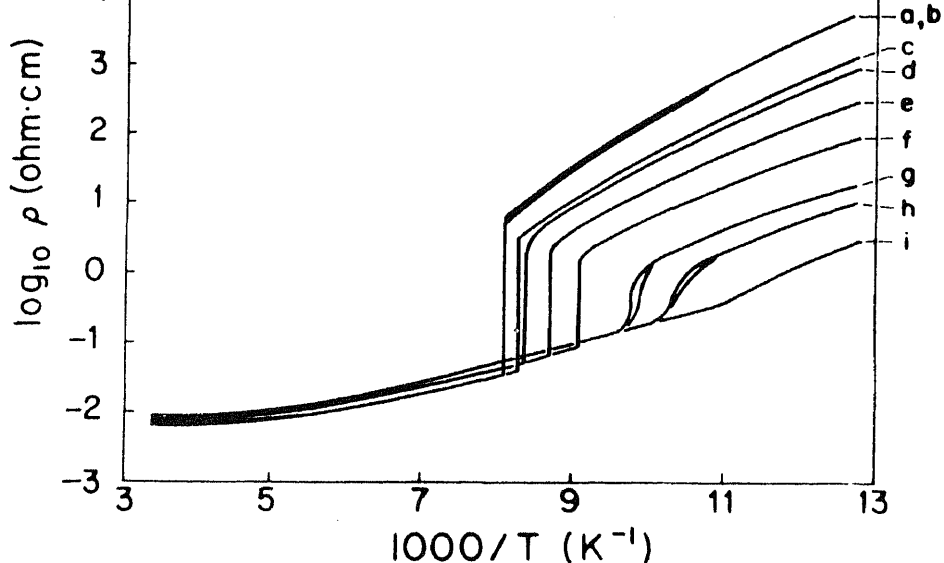


Figure 13. Resistivity of $\text{Fe}_{3(1-\delta)}\text{O}_4$ for samples with various δ . Data shown as plots of $\log \rho$ vs. $1/T$. Note the distinction between group A and group B specimens. Compositions: $\delta = -0.00053$ (a), -0.00017 (b), 0.00021 (c), 0.00018 (e), 0.00069 (d), 0.0017 (e), 0.0050 (g), 0.0068 (h), 0.0097 (i).

no systematic studies linking resistivity to compositional changes had previously been reported.

There have been many attempts to provide an adequate theoretical interpretation of the electron transport properties in magnetite. These may be roughly divided into several categories: (i) Cullen and Callen (1971, 1973) are representatives of a school which invokes band formation and then relies on the charge ordering mechanism at the transformation temperature to open up a gap in the density-of-states originally associated with the d -subbands. However, in this type of approach one must rely on strong electron-electron interactions and/or on quite small orbital overlaps between the constituent atoms to achieve a band-width small enough for the rather small charge carrier mobilities cited below. This avenue was carefully explored by Ihle and Lorenz (Ihle 1984; Ihle and Lorenz 1974, 1980; Lorenz and Ihle 1975a, b, 1979, 1982), who invoke SRO effects as a complication. The destruction of SRO with rising temperature simulates thermally activated conduction processes. As we stressed earlier, however, such SRO effects and their destruction have not been detected in our heat capacity measurements. In such circumstances it might be more appropriate to start out with a small-polaron (hopping) model of charge carriers. (ii) Srivastava (1983) as well as Hurd and collaborators (McKinnon *et al* 1981; Shiozaki *et al* 1981) have introduced an incoherent phonon-driven tunnelling mechanism to explain the observed electrical transport phenomena; the difficulty with this approach is that very unrealistic values of the various physical parameters must be introduced to obtain agreement with experiments. (iii) A very commonly championed view is that charge transport occurs via

measurements cited below, but a relatively persuasive, independent argument is provided through the simple expression $\sigma = neu$, relating the conductivity $\sigma \equiv 1/\rho$ to the density of charge carriers, n , their electric charge e , and their mobility u . Even for the extreme case $T = 300$ K, where $\sigma \approx 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$, one requires a mobility $u \approx 0.5 \text{ cm}^2/\text{v-sec}$ for charge carrier densities $n \approx 10^{22} \text{ cm}^{-3}$. Admittedly, this figure is close to the upper limit (Rathenau and Goodenough 1968) of mobilities associated with thermally activated charge transport, but for temperatures $T < 250$ K the conductivity has already become sufficiently small such that the requisite probabilities fall well below this upper limit. *A fortiori* this is even more the case below the Verwey transition temperature. One argument occasionally advanced against the small polaron mechanism is that data plots of the type shown in figure 13 do not form straight lines, such as are frequently encountered in the range $T < T_v$ for ceramic or polycrystalline material. However, contrary to misconceptions frequently quoted in the literature, departures from the Arrhenius behaviour do not signal a breakdown of the small polaron model. Rather, if one accepts charge transport as occurring by thermally activated displacement of carriers then conventional theory (Holstein 1954; Reik and Heese 1967) predicts a mobility $u(T)$ with a temperature dependence of the form

$$u \propto (\tau/T) \exp \{ -\eta \tanh(\hbar\omega_0/4kT) \}, \quad (11)$$

with

$$\tau^2 \equiv [\sin h(\hbar\omega_0/2kT)]/2(\hbar\omega_0/k)^2\eta, \quad (12)$$

in which there are two disposable parameters; the appropriate optical lattice frequency ω_0 and the degree of coupling η of the charge carriers to the lattice (roughly, the number of polarons clothing the electron or hole). These parametric degrees of freedom suffice to provide the needed curvature for a reasonable fit of the above equation to the data in figure 13. Only as an extreme limiting case does one obtain the usually-cited result $\ln u = -\hbar\omega_0/2kT + \text{constant}$, which is clearly inapplicable here. (iv) Lastly, a combination of small polaron band and hopping processes has been recently suggested to treat the electrical transport phenomena (Ihle and Lorenz 1985). Again, the gradual disappearance of sro with increasing $T > T_v$ was invoked, and this once more raises the questions as to the actual existence of short-range order configurations above T_v .

Seebeck coefficient measurements

We conclude with a brief summary of Seebeck coefficient (α) measurements. The data collected in the author's laboratory (Aragón *et al* 1985) are displayed in figure 14 as plots of α vs T . These results are similar in form to a more limited set published by Kuipers and Brabers (1976, 1979) on single crystals of magnetite or titanomagnetite containing small concentrations of Ti^{4+} close to ideal stoichiometry. Again, the data obtained here differ significantly from measurements reported for polycrystalline samples or ceramic types. Several features are noteworthy: (i) One may readily distinguish between the regions $T > T_v$ where the various Seebeck coefficients are nearly independent of temperature, and the region $T < T_v$ where α changes considerably with T . The near-constancy of α in the high temperature regime is difficult to reconcile with a band model involving itinerant charge carriers except for the special

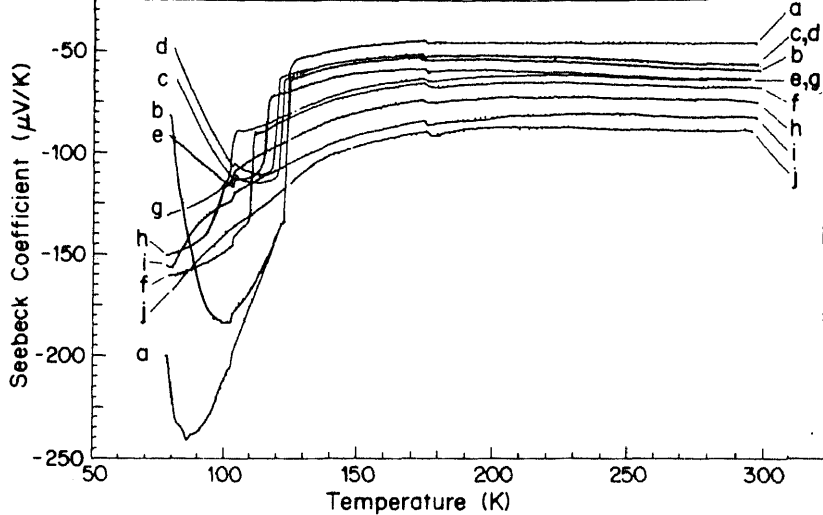


Figure 14. Seebeck coefficient data (α) for $\text{Fe}_{3(1-\delta)}\text{O}_4$ single crystal specimens with various δ . Data shown as plots of α vs. T . Compositions: $\delta \approx 0$ (a, b), 0.00017 (e), 0.00069 (a), 0.0018 (e), 0.0036 (f), 0.0052 (g), 0.0070 (h), 0.0099 (i), 0.012 (j). Note the distinction between group A and group B specimens.

case of an extrinsic band-type semiconductor for which the exhaustion range limit has been reached. However, the α values for such cases tend to be much larger than the values shown in figure 14. A much more natural explanation involves the use of the Heikes equation in the form (Van Zandt and Honig 1981)

$$\alpha \equiv -(k/e) \ln \{2[\text{Fe}_B^{3+}]/[\text{Fe}_B^{2+}]\}, \quad (13)$$

where k is Boltzmann's constant and $[\text{Fe}_B^{3+}]$ denotes the concentration ferric ions on B sites. For strictly stoichiometric material, $\alpha = -(k/e) \ln 2 = -60 \mu\text{V/deg}$, in reasonable agreement with the observed values. The constant α values shown in figure 14 change with δ roughly in conformity with (13), whereas Kuipers and Brabers (1976, 1979) encountered no such dependence. (ii) For $T > T_v$ the samples in group A undergo a discontinuity in α which moves to lower temperatures with increasing departures from ideal stoichiometry; the samples in group B exhibit an increasing dependence of α on T commencing at roughly 120 K. (iii) For $T < T_v$ the samples in group A pass through a minimum in α and then become less negative as the temperature is dropped. The samples in group B show a further decrease in α as T is diminished. These samples ultimately also must pass through a minimum since, by the third law of thermodynamics, α must come into the origin of coordinates with zero slope as $T \rightarrow 0$. Kuipers and Brabers (1976) reported a change in sign in α as the temperature is lowered, in contrast to the present findings (although such a change in sign might still be encountered at temperatures below the current set of measurements). They interpret their findings (similar to our results for group A specimens) on the basis of a two-carrier model involving small polarons of positive (hole-like) and negative (electron-like) charge.

Again, one should note that the results obtained with well-annealed single crystals differ qualitatively with those published in the literature on compacted polycrystalline specimens. This once more illustrates the problems inherent in the presence of grain boundaries and internal contacts in the latter group of samples.

Concluding comments

As has been repeatedly stressed, it is absolutely essential to develop adequate techniques for preparation and characterization of Fe_3O_4 samples in order to ensure that the various experimental measurements yield reliable results. Failure to appreciate this point in the past has led to confusion and to the publication of contradictory data in the literature. For thermodynamic and transport data the difference in experimental findings between adequately and inadequately prepared samples may be readily documented. It may equally well turn out that structural problems revealed by x-ray diffraction, electron diffraction, neutron diffraction, Mössbauer, or nuclear magnetic resonance measurements can be settled only after extensive reinvestigations with properly prepared specimens.

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Applications of molecular graphics to zeolite catalysts

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Abstract. The use of molecular graphics procedures to simulate hydrocarbon processes in zeolites is described. Calculations of heats of adsorption, activation energies for diffusion, and the location of solute molecules are considered, and a methodology for simulating an isomerisation reaction in a shape-selective zeolite catalyst is discussed.

Keywords. Zeolite catalysts; molecular graphics; computer simulation.

1. Introduction

For several decades, zeolites have enjoyed widespread use as water softeners, cation exchangers, and molecular sieves, and more recently they have been employed as industrial catalysts, for example in catalytic cracking (Rabo 1976). Of particular interest are the new, highly siliceous zeolites, which have a high affinity for hydrocarbons and are being used as shape-selective, heterogeneous catalysts.

Zeolites have the general formula $M_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]m\text{H}_2\text{O}$, where cations M , of valence n , compensate the negative charge of the zeolite framework. The latter is composed of SiO_4 and AlO_4 units, linked in such a way as to generate cages of molecular dimensions (up to ~ 11 Å), interconnected by windows, up to 8 Å in diameter (figure 1). The exchangeable cations, M , occupy a range of sites and are co-ordinated by oxygen atoms of the framework or by water molecules. The water can usually be driven out by heating under vacuum, leaving the cations with very low co-ordination numbers.

Computer graphics procedures are now being used in a variety of ways (Ramdas *et al* 1984):

- (1) to provide clear illustrations of the structural features of zeolites;
- (2) to model intergrowths and stacking faults;
- (3) to represent hydrocarbon diffusion pathways by means of energy-contoured diagrams.

Molecular mechanics models have also been developed for calculating the heats of adsorption and activation energies for diffusion of hydrocarbons in zeolites, using atom-atom potentials (Kiselev and Pham Quang Du 1981; Bezus *et al* 1984). We shall describe the applications of some of these methods to hydrocarbon adsorption and mobility in two important zeolites, faujasite and zsm-5. The former is used extensively

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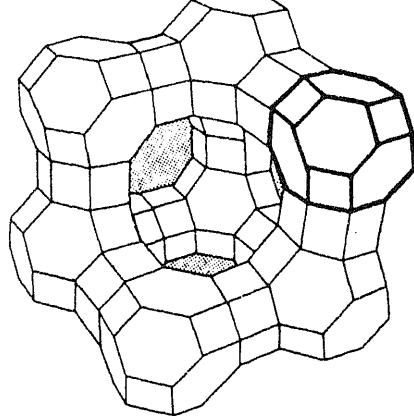


Figure 1. A view of the framework structure of zeolite-Y (faujasite).

as a cracking catalyst and the latter is being used for xylene isomerisation and the conversion of methanol to gasoline. We shall also examine the prospects for simulating catalytic reactions by using a combination of molecular mechanics and molecular orbital calculations.

2. Adsorption and activation energies

Work in this area was pioneered by Kiselev and co-workers (Kiselev *et al* 1978). The initial step involves the calculation of the interaction energy, $\phi(\text{tot})$, between the hydrocarbon and the zeolite. Several approximations are made:

- (1) the zeolite is assumed to be rigid and unperturbed by the presence of the solute molecule;
- (2) the hydrocarbon is assumed to be rigid and present in very low concentrations;
- (3) the interaction is described by a simple atom-atom potential. We have used a potential of the form:

$$\phi(\text{tot}) = \sum_{ij} \left[\frac{B}{r^{12}} - \frac{A}{r^6} + \frac{cq_i q_j}{r} \right]. \quad (1)$$

Values of A and B were determined semi-empirically (Kiselev *et al* 1978) by fitting experimental data for methane in zeolite-Y (one of the faujasite family) and the charges for the electrostatic term were obtained from molecular orbital calculations on both the hydrocarbons and the zeolites. Equation (1) must be sampled for all orientations of the hydrocarbon molecule, and at all positions in the cage, in order that the following integrations can be performed:

$$I_1 = \int_v \exp[-\phi(\text{tot})/RT] dv, \quad (2)$$

$$I_2 = \int_v \phi(\text{tot}) \exp[-\phi(\text{tot})/RT] dv. \quad (3)$$

The internal energy of adsorption, $\Delta U(\text{ads})$ can then be calculated according to the mean value theorem:

$$\Delta U(\text{ads}) = \bar{\phi}(\text{tot}) = I_1/I_2. \quad (4)$$

This gives the Boltzman-weighted interaction energy, thus accounting for entropy effects which distribute the molecule over an increasing number of sites as the temperature is increased. For example, though the minimum energy, $\phi(\text{min})$, of methane in zeolite-Y is -23.0 kJmol^{-1} , the molecule would only be expected to occupy the position with this energy at very low temperatures. At room temperature, however, $\bar{\phi}(\text{tot})$ is only -13.3 kJmol^{-1} .

In the table below, we compare the calculated and experimental adsorption energies for a series of hydrocarbons in zeolite-Y. As the molecules become larger, the energies increase. These values correspond to the energies of isolated molecules and are only valid at infinite dilution when intermolecular interactions can be ignored. We are currently working on the calculations at higher hydrocarbon loadings.

Activation energies are also of interest since they provide a means of rationalising some of the factors that control hydrocarbon diffusion in zeolites. Bezus *et al* (1984) calculated E by taking the difference between the minimum energy position, $\phi(\text{min})$, and the lowest barrier. Given that the molecules have only a low probability of occupying this site at ambient temperatures, the approach seems to be over-simplistic. We have chosen to take the difference between $\bar{\phi}(\text{tot})$ and the weighted-average energy of the molecule as it passes through the ring into the next cage, $\bar{\phi}(\text{ring})$. In the case of propane in zeolite-Y, the predicted value of the activation energy is 13 kJmol^{-1} , compared with the experimental value of $9.8 \pm 1.5 \text{ kJmol}^{-1}$ (Pfeifer 1981). One of the interesting conclusions that emerge from such calculations is that high activation energies often stem from large values for the heat of adsorption, rather than high ring barriers. A comparison of diffusion rates for 1,3,5-trimethylbenzene and its trimethylaniline analogue, in zeolite-Y, provides an interesting example. The sizes and shapes of the two molecules are almost identical, but their experimental activation energies are 38 and 71 kJmol^{-1} , respectively. Our calculation shows that much of this difference stems from the stronger interaction of the more polar amine molecule with the zeolite framework, leading to a substantially more negative value for $\bar{\phi}(\text{tot})$.

3. Experimental location of guest molecules

The treatment described in §2 provides a basis for predicting not only the energetics of adsorption, but also the location of adsorbed molecules. We have seen that, at ambient

Table 1. Internal energy of adsorption of hydrocarbons in zeolite-Y/ kJmol^{-1} .*

	Calcd.	Exptl.
CH_4	13.3	15.2
C_2H_6	21.5	23.3
C_3H_8	30.1	32.3
C_4H_{10}	35.2	37.4

* A K Nowak and A K Cheetham (unpublished results)

positions at low temperatures provide a useful test for the molecular graphics calculations since they should correspond to the positions of ϕ (min). There have been no single crystal diffraction studies of zeolite-adduct complexes, but, recently, several studies by high resolution powder neutron diffraction have been reported. These include the location of Xe in zeolite-rho (Wright *et al* 1984), CO in zeolite-A (Adams and Haselden 1984), benzene in zeolite-Y (Fitch *et al* 1985), and pyridine in zeolite-L (Wright *et al* 1985). In the latter instance, the molecule occupies a single site in the main channel, at 4K, coordinated to a potassium ion through the nitrogen of the pyridine ring (figure 2). Molecular graphics calculations (figure 3) predict the location and orientation of the molecule within 0.2 Å of the observed position, thus lending credence to the validity of both the experiment and the simulation.

4. Shape-selective catalysis in zsm-5

A great deal of recent interest has focused on the catalytic properties of the synthetic zeolite, zsm-5, first reported in 1972 (us patent 1972). Like most other zeolites, it owes its catalytic activity to the presence of Brønsted acid sites (protons attached to framework oxygen atoms) and its specificity to the shape and size of its channels (figure 4). One of the reactions for which it is used extensively is the isomerisation of xylenes (figure 5). An interesting feature of this reaction is that the useful product, paraxylene, which is used in the manufacture of polyesters, is significantly more mobile than the meta-derivative. A molecular graphics study of the mobility of *p*- and *m*-xylenes in zsm-5 reproduces this behaviour by means of a colour-contoured, potential

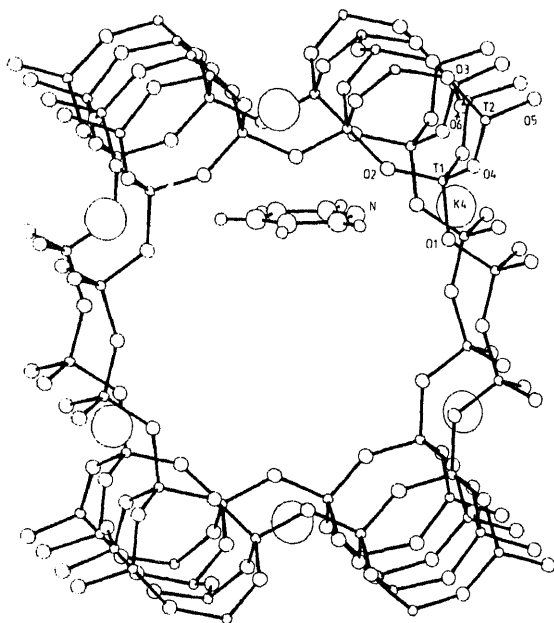


Figure 2. The location of pyridine in the main channel of potassium zeolite-L.

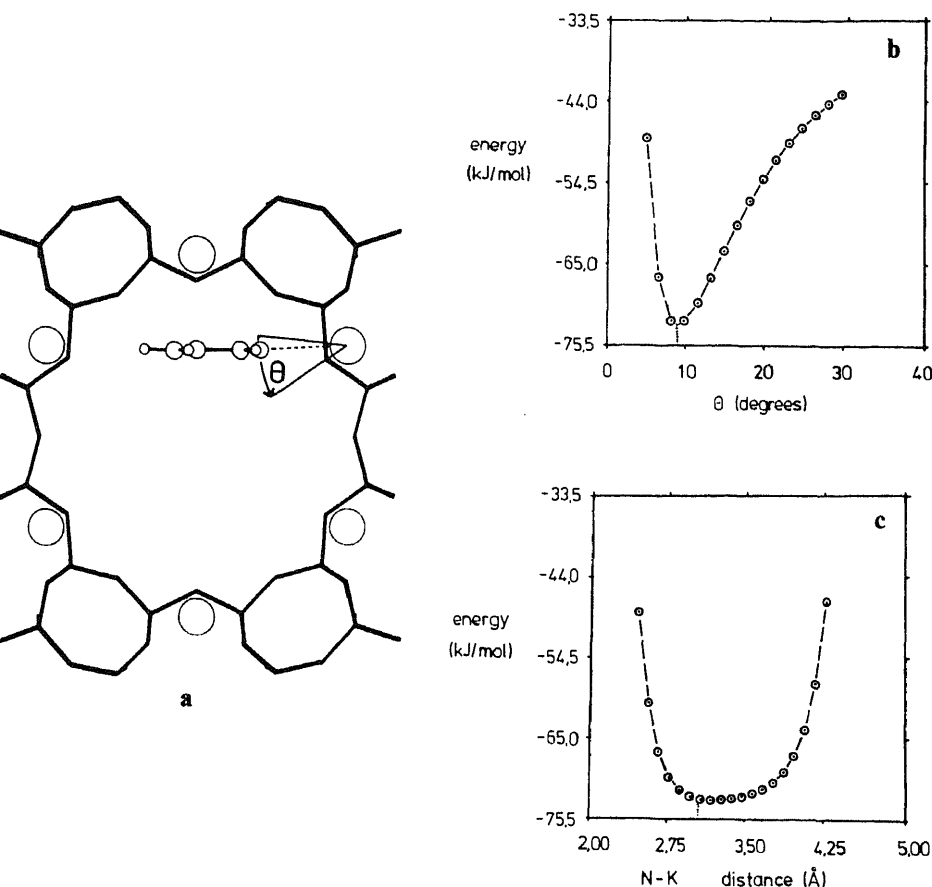


Figure 3. (a) A view of the pyridine molecule down [001] showing the angle θ which was varied for the calculations presented in (b). (b) The interaction energy between pyridine and zeolite-L as a function of angle θ , the observed angle is indicated by a dotted line. (c) The interaction energy as a function of the K(4)-N distance at $\theta = 8.8^\circ$; the observed position is again indicated.

energy diagram, which shows the variation of $\phi(\text{tot})$ as a function of the angular orientation and position of the molecule in the zeolite channel.

But perhaps the ultimate goal of the molecular graphics work is the simulation of a catalytic reaction by means of a combination of molecular graphics procedures, described here, and off-line molecular orbital calculations. We have now developed a methodology for this procedure and can illustrate it with some preliminary results on the xylene isomerisation. The initial step of the reaction, which is assumed without comment in other theoretical treatments (Corma *et al* 1979; Nebot *et al* 1981), is shown in figure 6. We have performed molecular orbital calculations (GAUSSIAN 80) on the four species A-D (for $X = \text{OH}$), and calculated the interaction energies, A-B and C-D, as described in §2. On this basis, the estimated activation energy for this initial step is

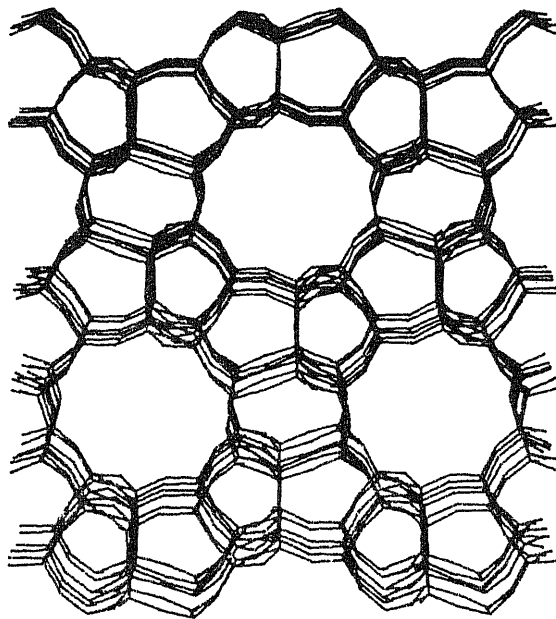


Figure 4. The framework structure of zsm-5, viewed down [010].

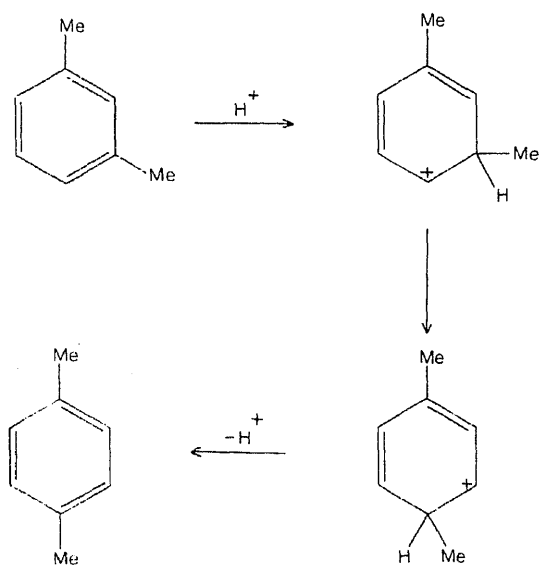


Figure 5. The isomerisation of xylenes.

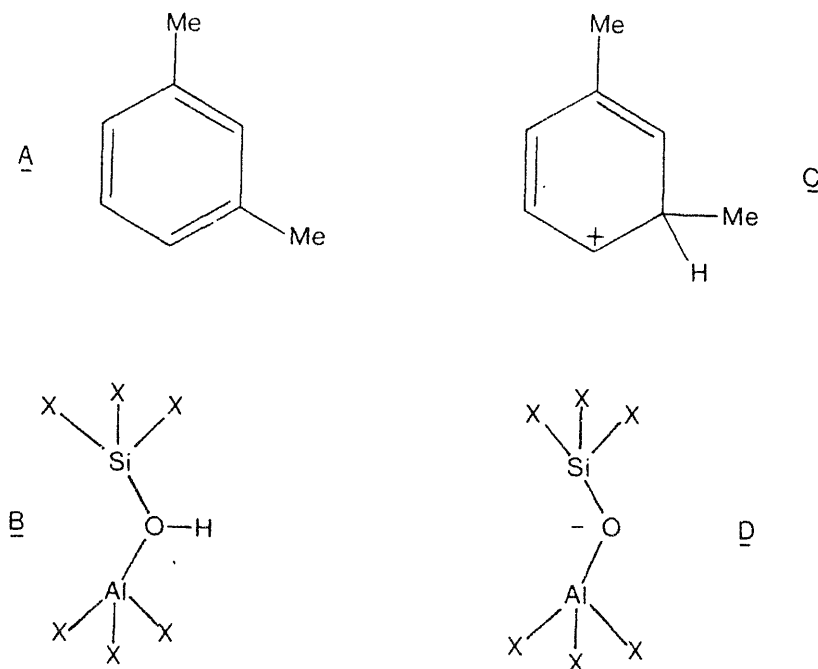
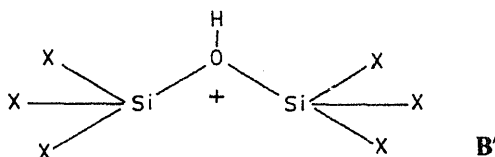


Figure 6. Species involved in the first step of isomerisation $A + B \rightarrow C + D$.



$\sim 634 \text{ kJmol}^{-1}$! If, however, we consider an acid site, B' , in which Al is replaced by Si, the O-H bond strength is much weaker, i.e. the acidity is much greater, and the activation energy is reduced by $\sim 540 \text{ kJmol}^{-1}$ to $\sim 90 \text{ kJmol}^{-1}$. The molecular orbital calculations require refinement by means of energy minimisation, but if the preliminary findings are confirmed, the results will have interesting implications in zeolite catalysis.

5. Conclusions

Recent work has shown that molecular graphics can play a vital role in enhancing our understanding of catalytic processes in zeolites, but a great deal remains to be done. Future work must explore some of the approximations that are currently being made, in particular the rigidity of both the framework and the guest molecules, but the techniques that are necessary to achieve this have been applied elsewhere and rapid

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Oxides with a tunnel structure characterized by a mixed framework of octahedra and tetrahedra

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Abstract. Oxides with a three-dimensional mixed framework built up from octahedra and tetrahedra are attractive owing to the possibility of forming large tunnels which can intersect as in the ionic conductors, or also to build anisotropic electronic conductors. The structural relationships between these oxides are analyzed here. Three classes of oxides are mainly studied here: mixed frameworks with tetrahedral silicate and germanate groups, oxides in which tetrahedral phosphates are involved and compounds involving silicophosphate groups. Other examples of mixed frameworks such as those involving GaO_4 tetrahedra and NbO_4 tetrahedra are also described.

Keywords. Mixed framework oxides; tunnel structure oxides; non-stoichiometric oxides.

1. Introduction

The properties of oxides characterized by a tunnel structure may be drastically influenced by the nature of their framework. For instance, the widest tunnels are observed for tetrahedral oxides: the zeolites are well known for their ion exchange properties and especially for their catalytic properties. On the other hand, octahedral oxides exhibit much smaller tunnels, but they offer the possibility of obtaining various physical properties; for instance the oxygen bronzes are known for their electron transport properties whereas bronzoids can be obtained which are ferroelectric or ionic conductors. In this respect, the synthesis of oxides with a mixed framework of octahedra and tetrahedra is attractive. Nevertheless, the number of these oxides is limited, owing to the weak ability of octahedra and tetrahedra to adapt to each other. The present review deals with the study of such frameworks. Mixed valence oxides resulting from the creation of anionic vacancies in an octahedral framework, such as oxygen-deficient perovskites will not be discussed here. Thus, the 'true' 'mixed frameworks' will be mainly built by association of SiO_4 , GeO_4 , PO_4 , NbO_4 , MoO_4 and GaO_4 tetrahedra with MO_6 octahedra, M being a transition element.

2. Mixed frameworks with tetrahedral 'silicate' and 'germanate' groups (Roedder 1951; Myashiro 1956; Robbins and Levin 1961; Gross *et al* 1965; Seifert and Schreyer 1967, 1969; Blasse and Bril 1970; Olsen and Bunch 1970; Shannon and Katz 1970; Choisnet *et al* 1972, 1976, 1977; Puscharovskii *et al* 1972; Evans *et al* 1973; Goreaud *et al* 1973; Groult *et al* 1976; Nguyen *et al* 1976, 1980; Chailleux *et al* 1978; Shannon *et al* 1978; Studer and Raveau 1978; Raveau 1979).

The great rigidity of the SiO_4 and GeO_4 tetrahedra makes for few oxides with a

tunnel structure built up from SiO_4 (or GeO_4) tetrahedra and MO_6 octahedra are known. Moreover most of the them are richer in the tetrahedral element than in the octahedral one. The oxides $\text{A}_{6-x}\text{M}_6\text{Si}_4\text{O}_{26}$ and $\text{A}_{6-x}\text{M}_6\text{Ge}_4\text{O}_{26}$ are the only ones which correspond to a ratio M/Si greater than one. Even for molar ratios M/Si ,

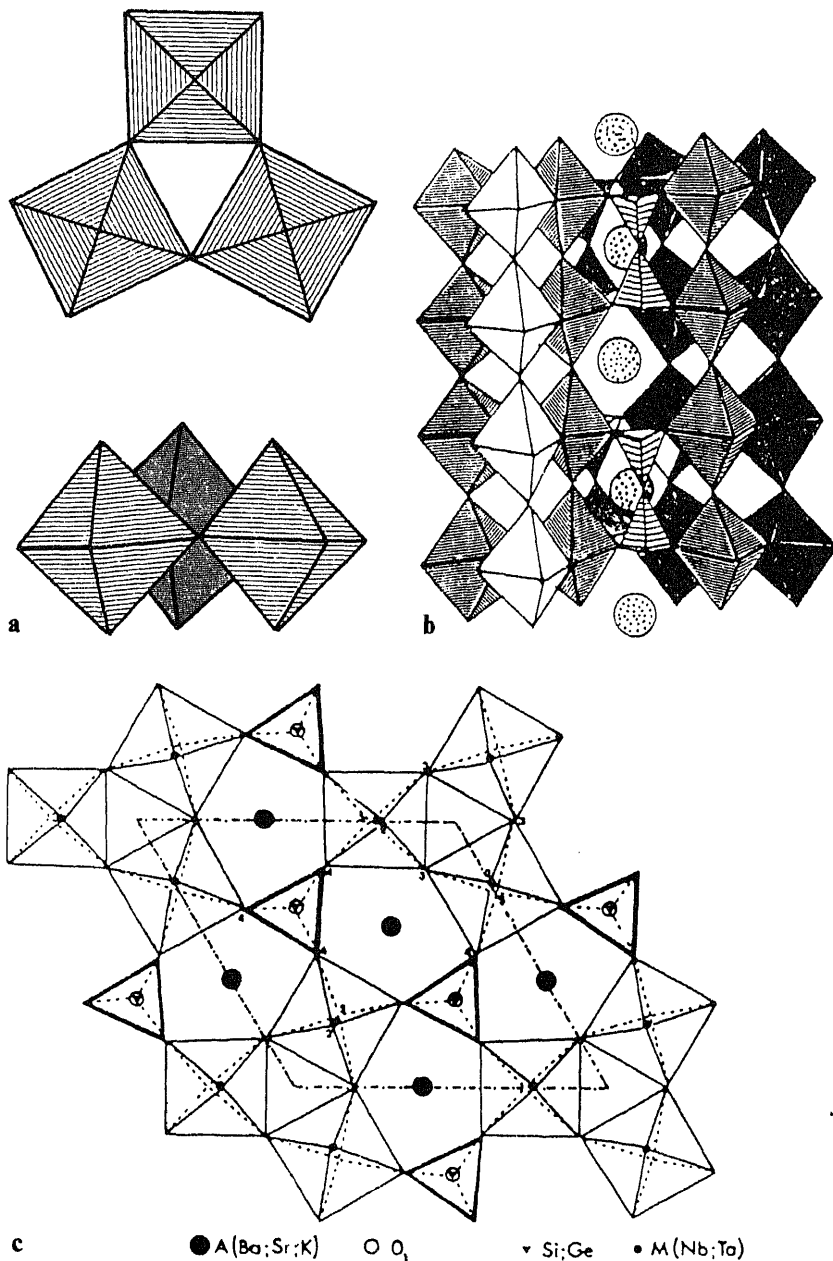


Figure 1. The siliconiobate and tantalate $\text{A}_3\text{M}_6\text{Si}_4\text{O}_{26}$ and $\text{K}_{6-2x}\text{Ba}_x\text{Ta}_6\text{Si}_4\text{O}_{26}$. (a) the octahedral units M_3O_{15} , (b) the triple files of octahedra and the Si_2O_7 groups, (c) projection of the structure on to the (001) plane.

smaller than one, few oxides with a tunnel structure are known; three examples will be described here: the benitoïtes $AMSi_3O_9$ and $AMGe_3O_9$, the milarites $A_xM_3M_2Si_{12}O_{30}$ and the silicates $Na_5MSi_4O_{12}$.

The siliconiobates and tantalates $A_3M_6Si_4O_{26}$ ($A = Ba, Cr, M = Ta, Nb$) $K_{6-x}Ba_xTa_6Si_4O_{26}$ and the silicogermanates $K_6M_6Si_{4-x}Ge_xO_{26}$ ($M = Ta, Nb$) form an important family of tunnel structures. In these hexagonal oxides the $M_6Si_4O_{26}$ framework is built up from octahedral units ' M_3O_{15} ' (figure 1a) and disilicate groups sharing their corners. Along c the octahedral units ' M_3O_{15} ' share their corners, forming infinite triple files of octahedra (figure 1b) identical to those observed in the hexagonal tungsten bronze structure (HTB); laterally, in the (001) plane the octahedral files share their corners with Si_2O_7 (or Ge_2O_7) groups whose ternary axis is parallel to c (figure 1c). This host lattice forms pentagonal tunnels very similar to those observed for the tetragonal tungsten bronze and characterized by angles of 90° and 120° . In these tunnels the K^+ and Ba^{2+} ions are located at two different levels along c (figure 1b); the difference between these two sites is due to the presence in one of them of the bridging oxygen of the Si_2O_7 group at the same level; consequently two sorts of coordinations are observed for the A ions (10+3) and (10+5). The important deviation from stoichiometry on the A cations, with x values ranging from 0 to 3, is another common point with the TB structure. The boroniobate and tantalate $KM_3B_2O_{12}$ ($M = Ta, Nb$) have got a very similar framework, in spite of their different formation. This latter structure is simply deduced from the $M_6Si_4O_{26}$ framework by replacing each disilicate group by two triangular BO_3 groups, which ensure the cohesion between the octahedral files. Thus the $M_6B_4O_{24}$ framework (figure 2) is very similar to the one of $K_6M_6Si_4O_{26}$. The great flexibility of such a structure is confirmed by its possible intergrowth with the hexagonal oxide $A_3M_8O_{21}$ ($A = Ba, Sr, K; M = Nb, Ta, Ti$). This latter oxide represented by the composition $Ba_3Nb_4Ti_4O_{21}$, has its octahedral framework formed of octahedral units M_6O_{24} resulting from the association of two ' M_3O_{15} ' units by the edges of their octahedra (figure 3). Along c the M_3O_{15} units share the corners of their octahedra forming infinite triple files of octahedra whereas in the (001) plane these files share their corners with octahedra whose ternary axis is parallel to c (figure 4). Consequently, the (001) planes of both frameworks exhibit a bidimensional accord. This similarity between the two structures allows the building up of a series of intergrowths $(A_{6-x}M_6Si_4O_{26})_n \cdot (A_3M_8O_{21})_m$ as shown on figure 5 which corresponds to $K_{10}Nb_{22}Ge_4O_{68}$ ($n = 1, m = 2$).

The numerous hexagonal silicates and germanates $AMSi_3O_9$ and $AMGe_3O_9$,

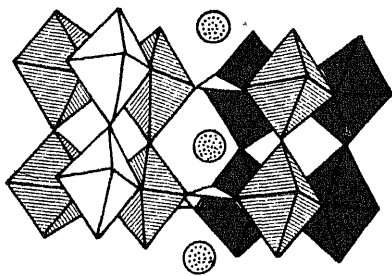


Figure 2. The boroniobate $K_3Nb_3B_2O_{12}$: the triple files of octahedra and their connection with the BO_3 triangles.

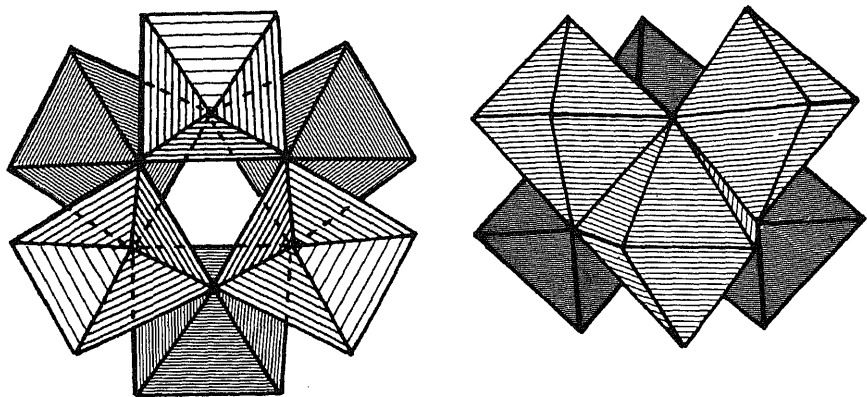


Figure 3. The structural unit ' M_6O_{24} ' resulting from the association of two ' M_3O_{13} ' units.

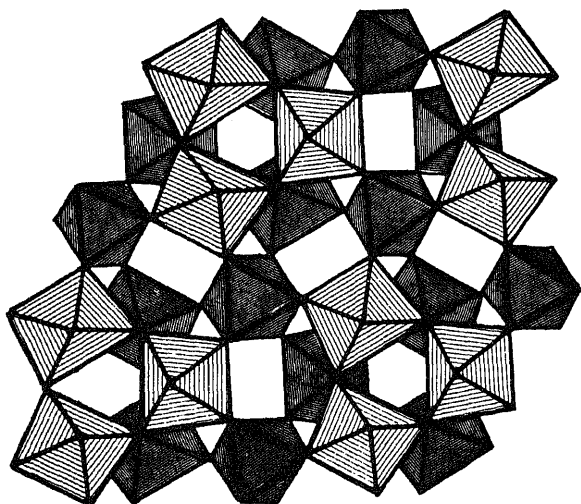


Figure 4. Projection of the structure of the hexagonal oxides $K_3M_8O_{21}$ on to the (001) plane.

($A = K, Rb, Tl, Ba$; $M = Ta, Nb, Sn, Ti$) belonging to the benitoite family result from the ability of MO_6 octahedra to adopt a tetrahedral framework. Their framework is built up of Si_3O_9 (Ge_3O_9) rings which are linked through isolated MO_6 octahedra (figure 6) forming wide tunnels where the A ions are located. It must be pointed out that no deviation from stoichiometry has been observed for those oxides in spite of the presence of tunnels.

The silicates of the milarite family $A_xM_3M'_2Si_{12}O_{30}$ ($A = K, Na, Ba, Rb$; $M = Zn,$

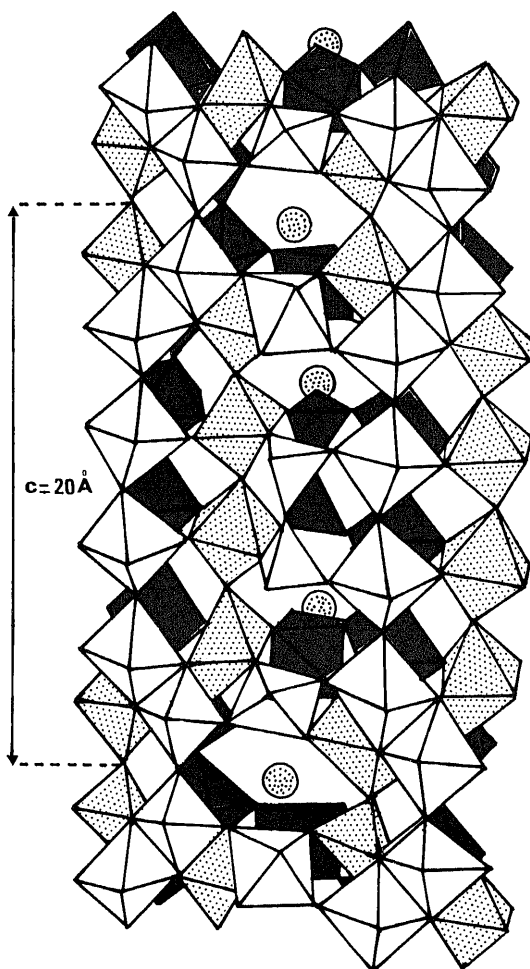
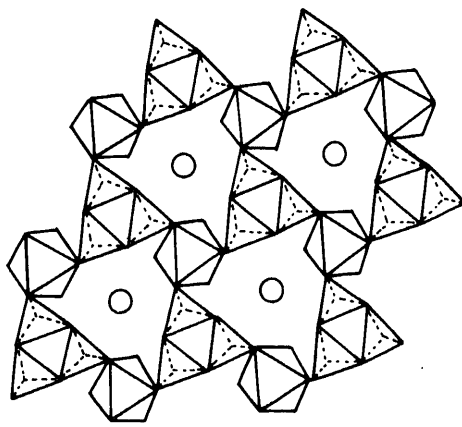


Figure 5. Structure of the oxide $\text{K}_{10}\text{Nb}_{22}\text{Ge}_4\text{O}_{68}$, the second member of the inter-growth $(\text{A}_3\text{M}_8\text{O}_{21}) \cdot \text{A}_{6-x}\text{M}_6\text{Ge}_4\text{O}_{26}$.



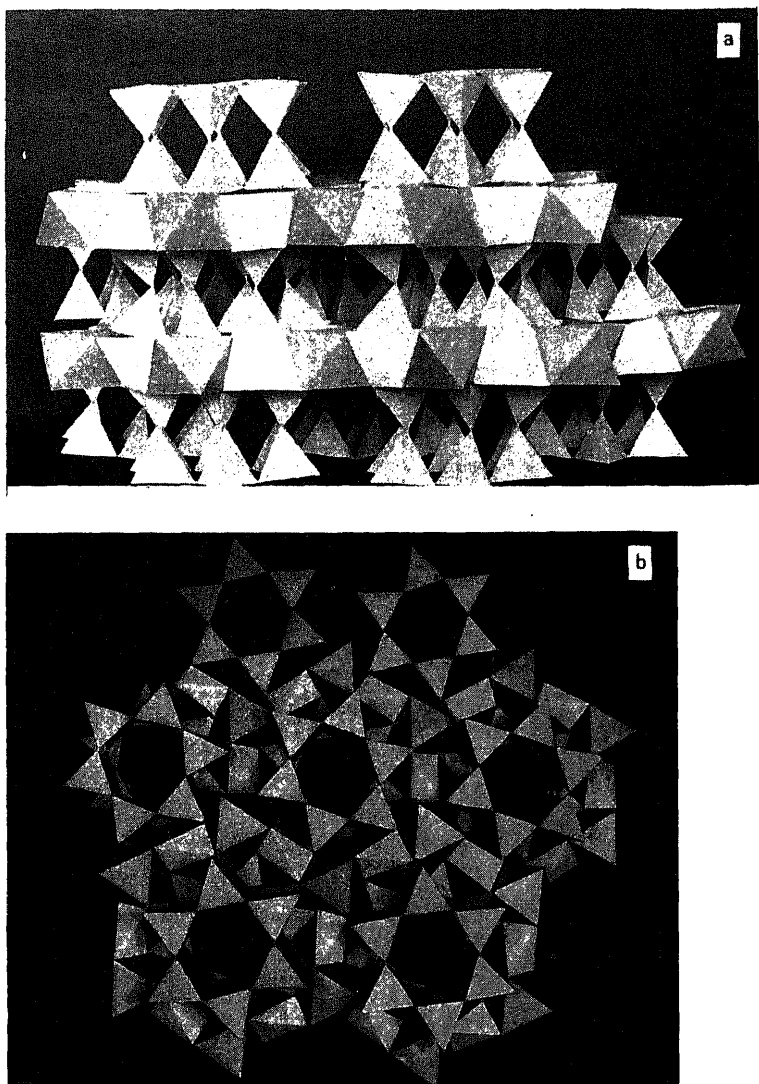


Figure 7. The milarite host-lattice $M_3M_2Si_{12}O_{30}$: (a) view along the direction perpendicular to c , (b) view along c .

along c delimits two sorts of tunnels, inside and outside of the crowns respectively, where the A ions are located (figure 7b).

The important family of ionic conductors $Na_5MSi_4O_{12}$ ($M = Fe, In, Se, Y$ and $Ln = Ln$ to Sm) are also characterized by a mainly tetrahedral framework. The host lattice of these oxides which is formed of tetrahedral rings $Si_{12}O_{30}$, connected through MO_6 octahedra (figure 8) delimits two sorts of tunnels, inside and outside the rings respectively. It has been shown that the Na^+ ions do not delimit these tunnels, as in the

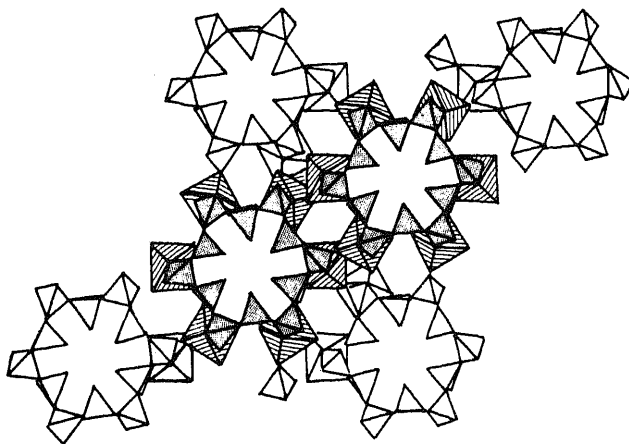


Figure 8. Projection of the structure of the ionic conductor $\text{Na}_5\text{MSi}_4\text{O}_{12}$ on to the (001) plane.

3. Mixed frameworks with tetrahedral 'phosphate' groups (Magneli 1948; Kierkegaard 1962; Kihlberg 1963; Middlemis 1978; Giroult *et al* 1981, 1982; Domenges *et al* 1982, 1983, 1984, 1985; Hervieu and Raveau 1982, 1983; Labbe *et al* 1982; Leclaire *et al* 1983, 1985b; Benmoussa *et al* 1984; Goreaud *et al* 1985; Hervieu *et al* 1985; Masse *et al* 1985)

The PO_4 tetrahedra seem to adapt octahedral frameworks much more easily than the SiO_4 groups. Nevertheless the nature of M ions of the octahedral lattice is important: most of the three-dimensional frameworks can be obtained by association of PO_4 tetrahedra with WO_6 , MoO_6 and VO_6 octahedra.

The numerous family of phosphate tungsten bronzes can be considered as one of the most representative examples of adaptability of phosphate groups to an octahedral framework which is in fact that of ReO_3 . The relationships between the different series of phosphate tungsten bronzes can easily be understood by considering the great ability of the PO_4 tetrahedron to replace an octahedron without changing the geometry of the ReO_3 -type framework. The starting point of the structural chemistry of these bronzes can be represented by layers of the ReO_3 -type which are one octahedron thick along $[001]_{\text{ReO}_3}$ and n octahedra wide along $[100]_{\text{ReO}_3}$, bordered by simple PO_4 tetrahedra along the latter direction (figure 9a). Two ways of association of these layers along the direction perpendicular to their mean plane can be considered. In the first one two adjacent identical layers are stacked in such a way that WO_6 octahedra share their corners with other octahedra only, leading to the formation of diphosphate groups (figure 9b), whereas in the second manner two successive layers are stacked up by corner-sharing their polyhedra such that two tetrahedra belonging to two different layers are never connected (figure 9c). Thus, two sorts of slabs can be distinguished: ReO_3 -type slabs bordered with diphosphate groups which can also be represented by figure 9a, and ReO_3 -type slabs bordered by simple PO_4 tetrahedra stacked according to figure 9c, leading to the scheme presented in figure 9d.

The lateral connection of the ReO_3 -type slabs bordered with diphosphate groups can be carried out in two different ways (figure 10) which differ from each other only by a

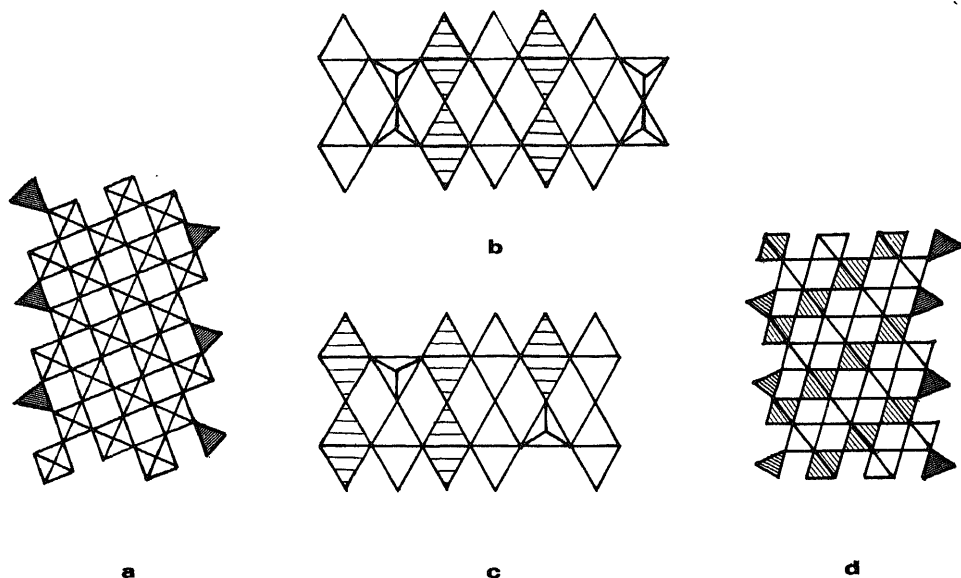


Figure 9. ReO_3 -type slabs of the phosphate bronzes bordered with (a) PO_4 tetrahedra; their two ways of stacking leading to (b) diphosphate groups, and (c) single PO_4 tetrahedra. (d) The other representation of the stacking according to (c).

rotation of 180° of one layer out of two around the direction perpendicular to the slabs. This first type of association leads to the diphosphate tungsten bronze with hexagonal tunnels (DPTB_H) (figure 10b) and to the diphosphate tungsten bronze with pentagonal tunnels (DPTB_P) (figure 10c) respectively. The DPTB_H , $A_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ ($A = \text{K, Rb, Tl, Ba}, x \sim 1$), thus form an important family whose different m -members differ only by the number m of octahedra which characterize the ReO_3 -type slab; the size of their hexagonal tunnels which are characterized by angles of 120° and 90° , makes them comparable to the HTB. The DPTB_P , whose composition may be formulated as $(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ or $\text{K}_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$, have never been isolated in the form of pure samples, but have been observed as microcrystals by high resolution electron microscopy. Semi-regular sequences are often observed involving diphosphate planes as shown by the micrograph of figure 11a; the structure of such junctions (figure 11b) forming pentagonal tunnels was confirmed by simulation (figure 11c).

The lateral connection of the ReO_3 -type slabs bordered with simple PO_4 tetrahedra can also be connected in two different ways (figure 12) which differ also from each other only by the rotation of one slab out of two by 180° around an axis perpendicular to the slabs. Consequently two monophosphate bronze families have been isolated: the monophosphate tungsten bronzes with pentagonal tunnels (MPTB_P) $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ (figure 12b) and the monophosphate tungsten bronzes with hexagonal tunnels (MPTB_H), $A_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$ ($A = \text{Na, K}, x = 2$) (figure 12c); as for the DPTB series the different members of these series differ from one another only by the number m of octahedra which determine the width of the ReO_3 -type slabs.

The great flexibility of such mixed frameworks are shown by the HREM study of the barium DPTB_H . For instance besides the perfect integral m -members (figure 13), one observes for non integral m -values intergrowths of different m -members (figure 14), and

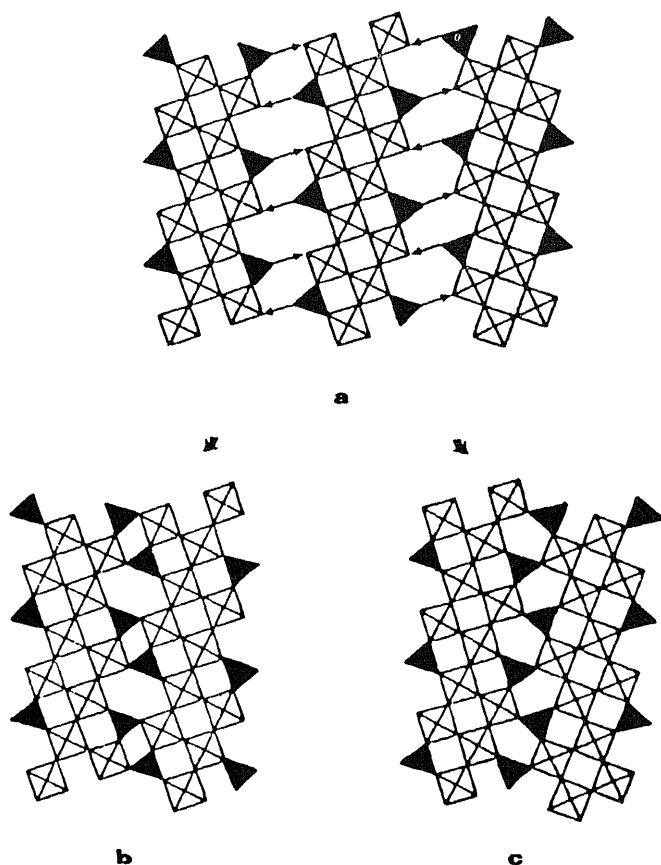
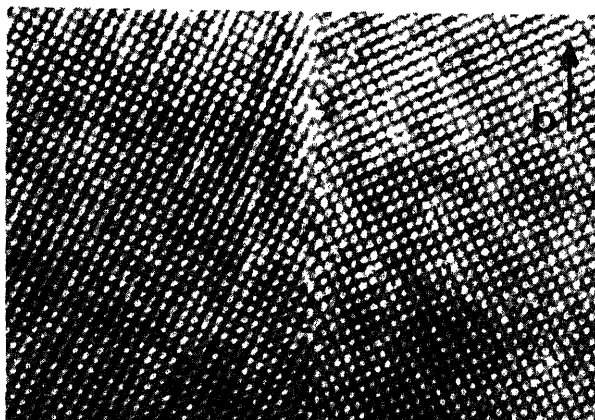
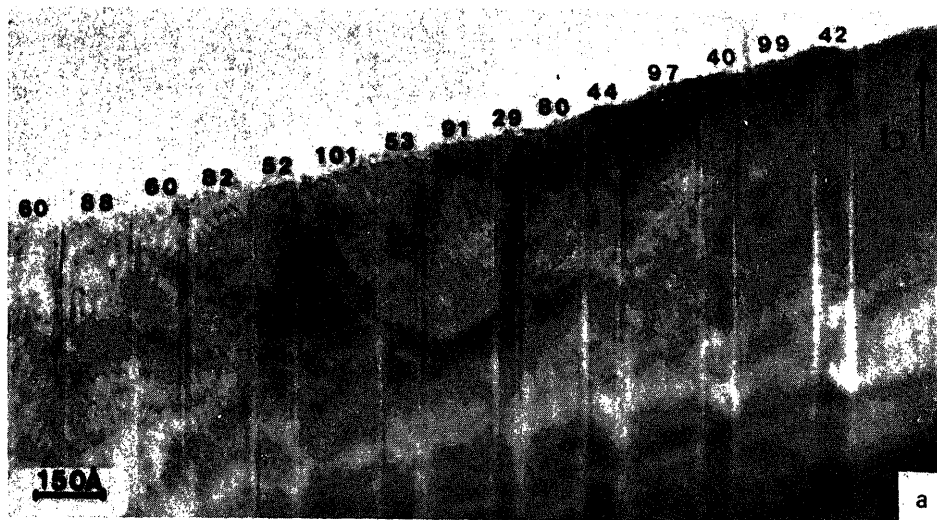


Figure 10. Lateral connection of the ReO_3 -type slabs bordered with (a) diphosphate groups, leading to the diphosphate tungsten bronzes with (b) hexagonal tunnels (DPTB_H), and to (c) the diphosphate tungsten bronzes with pentagonal tunnels (DPTB_P).

the possibility of stopping the propagation of the phosphate planes leading to wide ReO_3 -type regions (figure 15), or of shifting phosphate planes with respect to one another in two adjacent regions of a crystal (figure 16). It is worth noting that the presence of one diphosphate group in the ReO_3 matrix leads to the formation of dislocations (figure 17). The adaptability of those mixed frameworks to the shear structures is also remarkable as shown from the regular lateral intergrowth of the $\{102\}$ C.S. planes with diphosphate planes (figure 18) and more complex associations of different shear planes with diphosphate planes as shown in figures 19 and 20.

The great ability of the WO_6 octahedra to be connected to PO_4 tetrahedra to form a tunnel structure is also found in the oxides $\text{P}_8\text{W}_{12}\text{O}_{52}$, $\text{CsP}_8\text{W}_8\text{O}_{40}$ and NaWPO_6 . The host lattice of the oxide $\text{P}_8\text{W}_{12}\text{O}_{52}$ (figure 21) formed of ribbons of ReO_3 -type connected to P_2O_7 groups, shows that various tunnels—with a pentagonal and hexagonal section—can be empty as in MPTB_P . The bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$ whose framework is built up from ReO_3 -type columns, connected through diphosphate groups is remarkable for its octagonal tunnels (figure 22) which are among the widest known in oxides with a mixed framework. Nevertheless no deviation from stoichiometry has

been observed for the Cs^+ ion located in the tunnels of this latter oxide. In the same way the phosphotungstate NaPWO_6 and the isomorphous oxide NaPMoO_6 , are stoichiometric in spite of the fact that they exhibit a tunnel structure. The host lattice of these compounds is characterized by infinite mixed chains in which one octahedron alternates with one PO_4 tetrahedron (figure 23a); laterally these chains are linked together in such a way that every tetrahedron of one chain shares one corner with an octahedron of the adjacent chain forming an helicoidal arrangement of the polyhedra (figure 23b). The structure of the phosphomolybdates $\text{PbMo}_2\text{P}_2\text{O}_{12}$ and



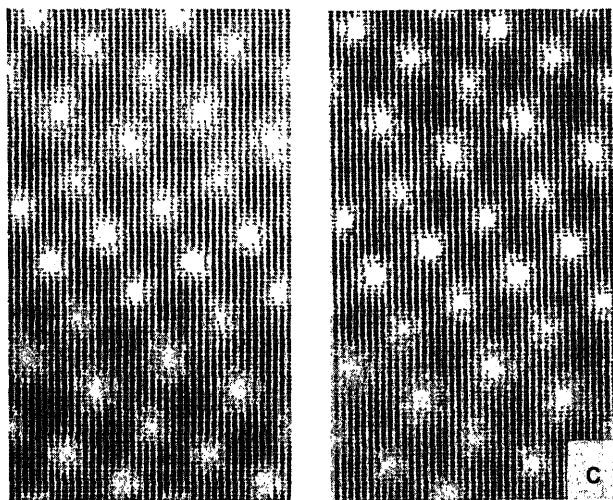


Figure 11 (c).

Figure 11. Diphosphate tungsten bronzes with pentagonal tunnels in the system $(P_2O_4)_2(WO_3)_{2m}$: (a) low resolution image showing a regular distribution of WO_3 -slabs in the mean sequence 48-91 (b) HREM micrograph of the twin boundary in a $(P_2O_4)_2(WO_3)_{2m}$ crystal and (c) its fit with the calculated image for a $-400 \text{ \AA}$ defocus value.

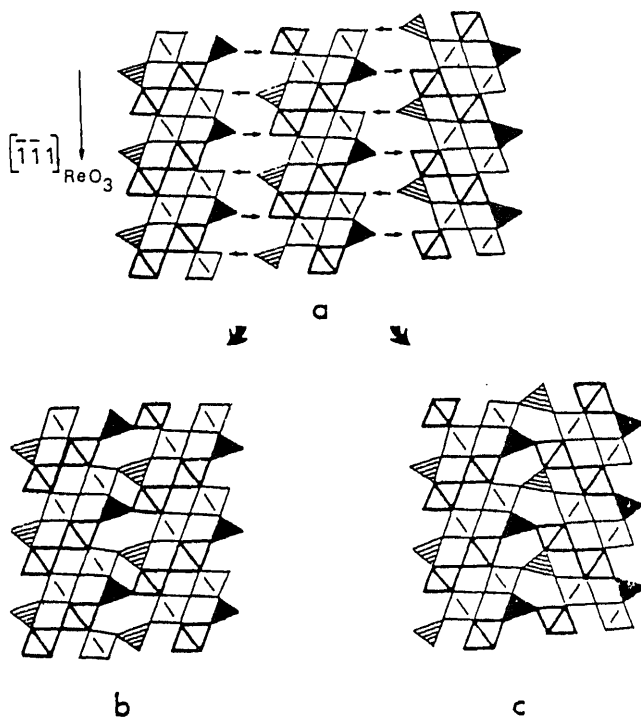


Figure 12. Lateral connection of the ReO_3 -type slabs bordered with (a) single PO_4 tetrahedra, leading to (b) the monophosphate tungsten bronzes with hexagonal tunnels

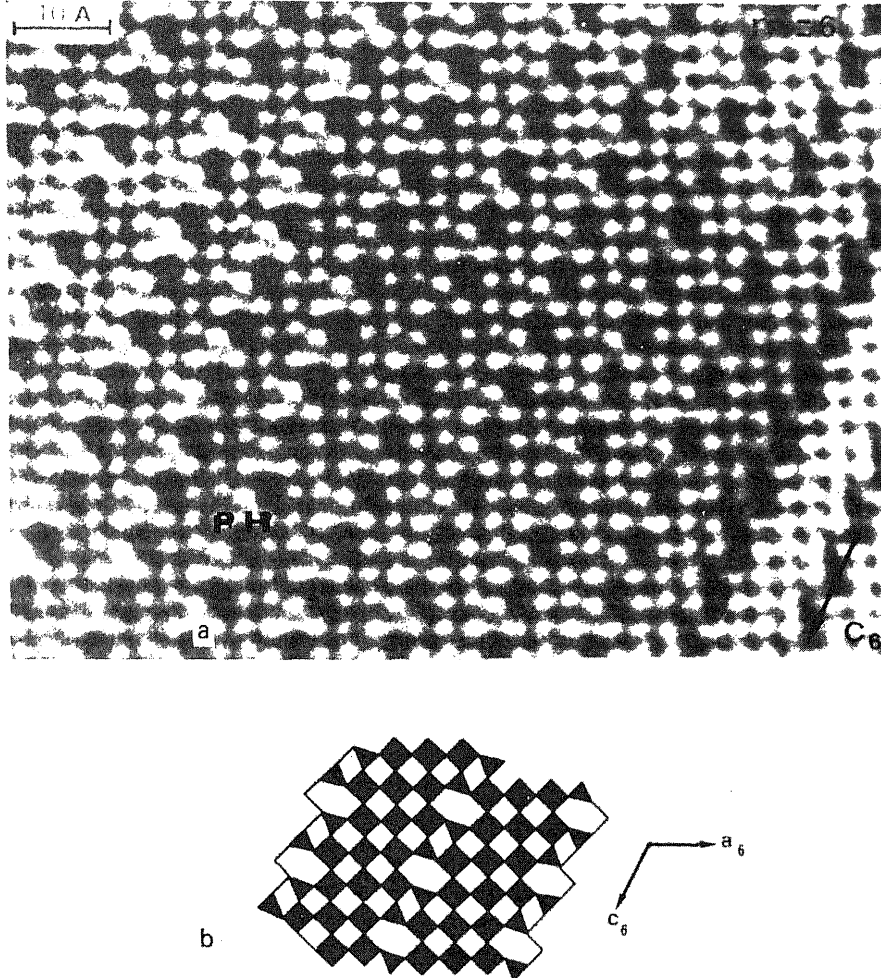


Figure 13. (a) An HREM image of $\text{Ba}(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{12}$ ($m = 6$) projected down the $[010]$ direction at about $-600 \text{ \AA}$ underfocus. The white spots correspond to perovskite (P) and hexagonal (H) tunnels respectively. (b) Idealized structure of $m = 6$.

$\text{BaMo}_2\text{P}_2\text{O}_{12}$ is very similar to that of NaPWO_6 : the mixed chains of octahedra and tetrahedra form the same helicodal arrangement. The main differences concern the tilting and the distortion of the polyhedra.

The recent study of the ternary oxides of molybdenum and phosphorus shows that molybdenum can also participate in the formation of tunnel structures involving PO_4 tetrahedra. $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ and $A\text{Mo}_2\text{P}_3\text{O}_{12}$ ($A = \text{K}, \text{Ti}, \text{Rb}$) characterized by the pentavalent and tetravalent states of molybdenum are two examples of such structures. The host lattice of the oxide $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ is very complex (figure 24); it is built up from corner-sharing MoO_6 octahedra, PO_4 tetrahedra and diphosphate groups P_2O_7 .

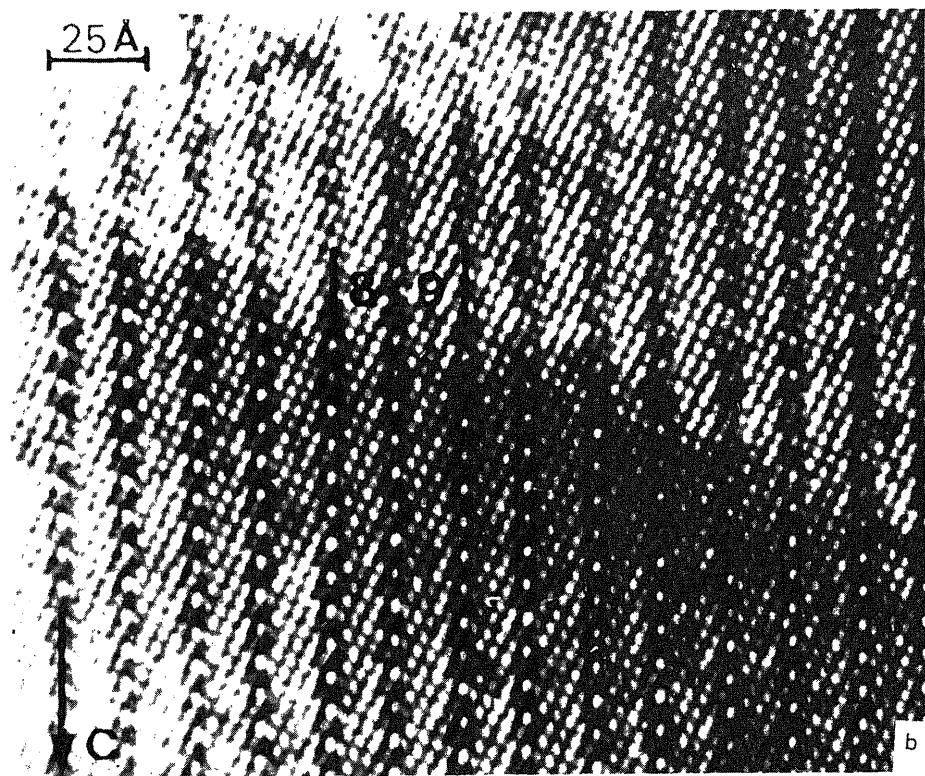
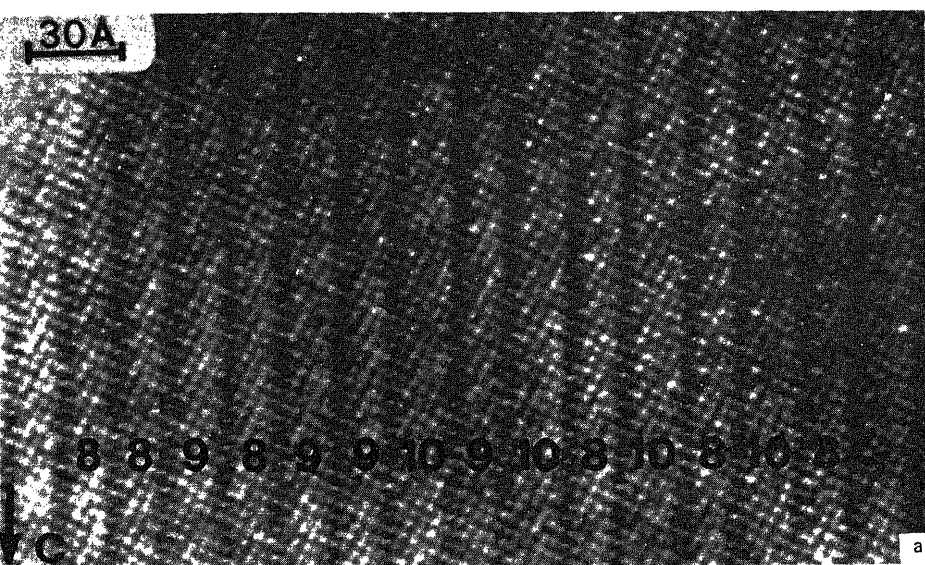


Figure 14. HREM images of intergrowths in the $\text{DPTB}_H\text{Ba}(\text{P}_2\text{O}_4)_4(\text{WO}_3)_{2m}$: (a) disordered crystal corresponding to the intergrowth of $m = 8, 9$ and 10 members. (b) ordered intergrowth

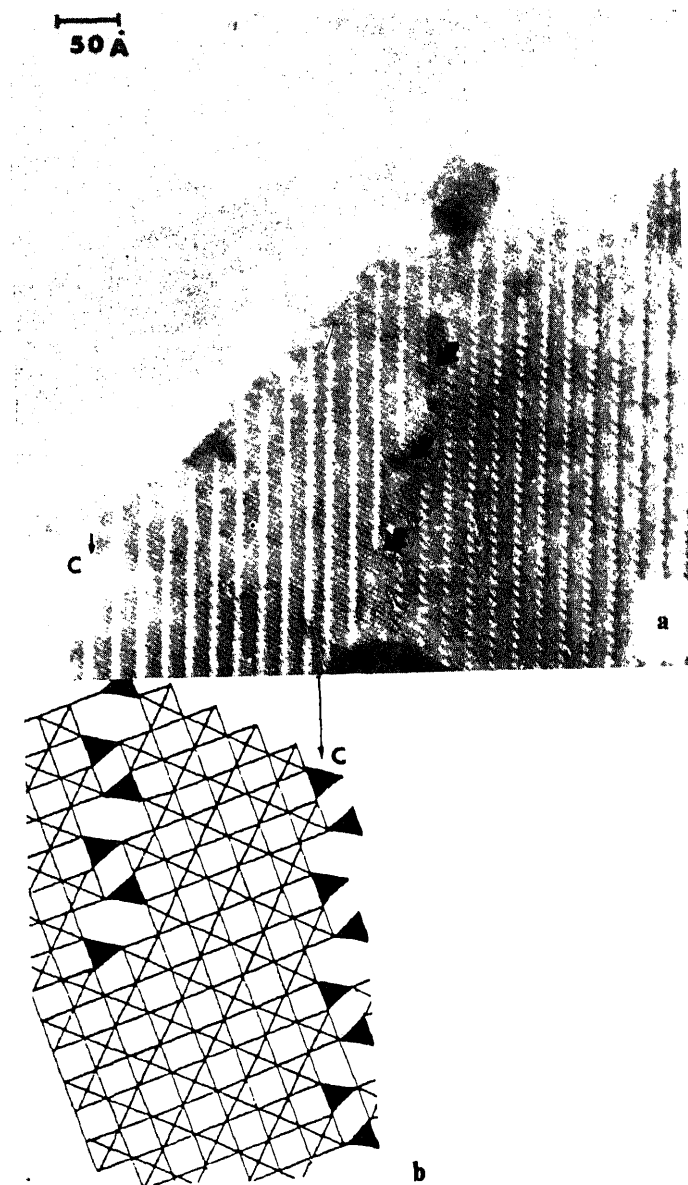
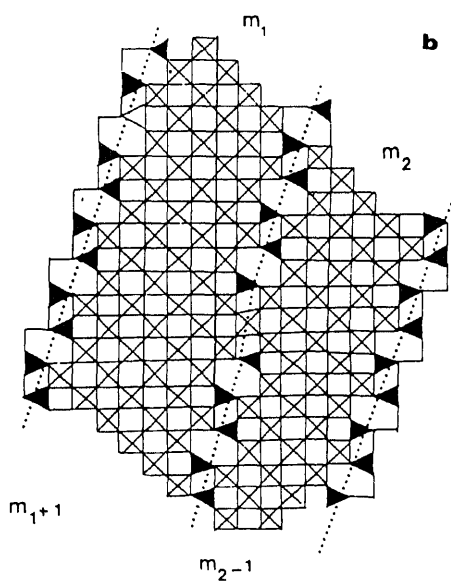
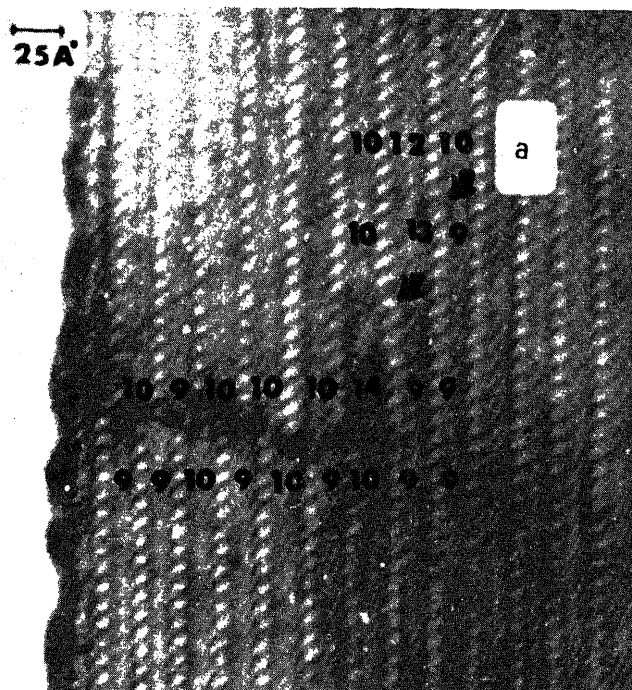


Figure 15. (a) Termination of the 'diphosphate rows' in an $m = 11$ member of the potassium DPTB_H , and (b) idealized drawing of such a phenomenon.



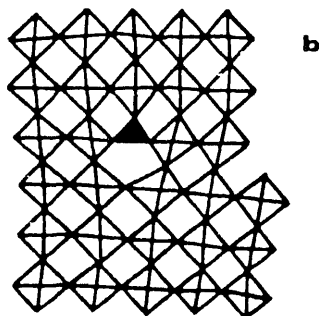
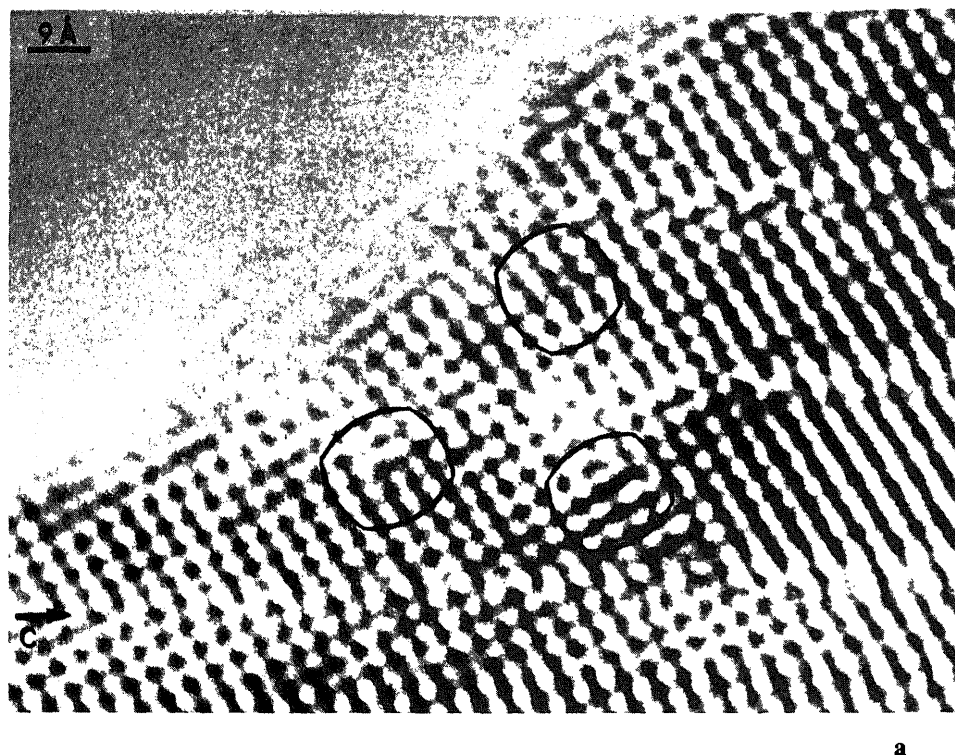
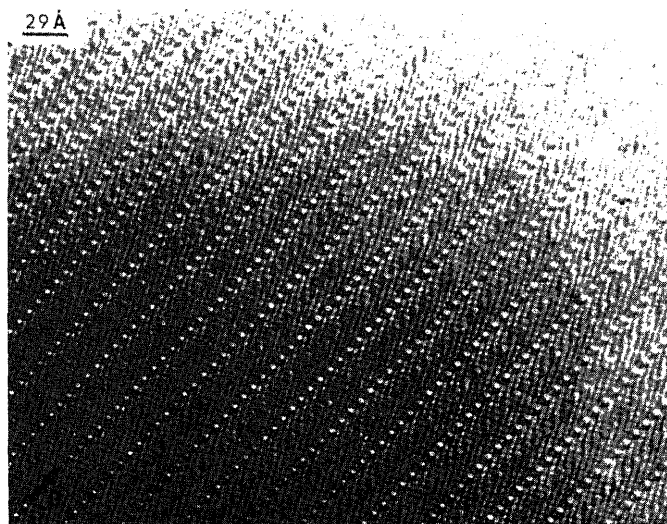


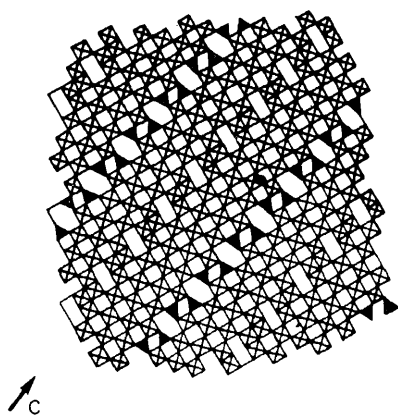
Figure 17. HREM micrograph showing (a) the formation of a dislocation in a ReO_3 matrix, due to (b) the presence of a diphosphate group.

a MoO_5 pyramid. The size of the tunnels where the K^+ ions are located is close to those observed in octahedral structures.

The molybdenophosphate $\text{AMo}_2\text{P}_3\text{O}_{12}$ has its host lattice built up from corner-sharing PO_4 tetrahedra, diphosphate groups P_2O_7 and MoO_6 octahedra forming hexagonal tunnels where the A ions are located (figure 25). This structure is characterized by chains of polyhedra in which units of two corner-sharing octahedra alternate with P_2O_7 groups as in the bronze $\text{CsP}_2\text{W}_3\text{O}_{12}$. The similarity of this



a



b

Figure 18. (a) Micrograph of a thin crystal of $\text{DPTB}_H \text{K}(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ ($m = 19$) showing a quasi regular sequence of $\{102\}$ CS planes and (b) idealized drawing of the corresponding structure.

structure with the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$ is shown in figure 26. In both structures one observes similar double chains (figure 26b) in which every P_2O_7 group shares two corners with a Mo_2O_{11} unit formed of two octahedra. However, the relative orientation of two successive chains is different in both structures. Moreover the $\text{P}_8\text{W}_8\text{O}_{40}$ framework (figure 26c) is only built up from these double chains, whereas in the $\text{Mo}_2\text{P}_3\text{O}_{12}$ host lattice these double chains are linked through simple PO_4 tetrahedra (figure 26b). The structure of $\text{TiMo}_2\text{P}_3\text{O}_{12}$ is also closely related to that of the hexagonal tungsten bronze of Magneli.

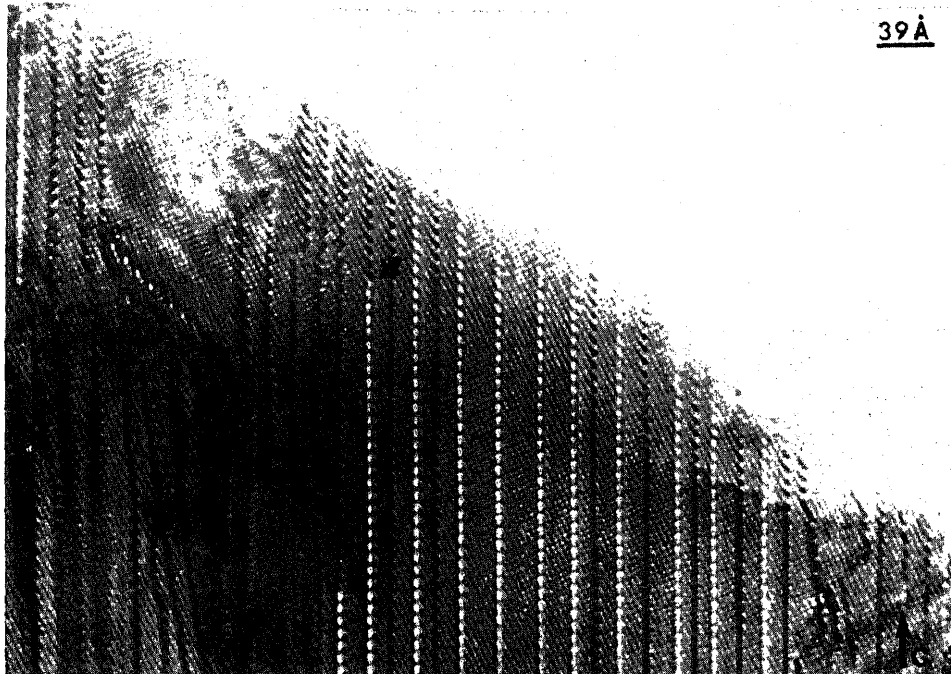


Figure 19. Complex association of diphosphate planes and crystallographic shear planes showing: lateral intergrowths of $\{102\}$ CS planes and diphosphate planes, longitudinal intergrowths of $\{102\}$ CS planes and diphosphate planes, formation of $\{103\}$ CS planes in the ReO_3 -type matrix.

Consideration of this host lattice along another direction shows that it can be described as a stacking of identical layers (figure 27) of polyhedra which are characterized by hexagonal rings deduced from those of HTB by replacing two octahedra by two PO_4 tetrahedra.

The oxide $\text{V}_2\text{P}_2\text{O}_9$ represents the limit case of the tunnel structures characterized by a mixed framework. In such a lattice (figure 28) chains of ReO_3 -type are associated by the edges of their octahedra forming pairs. These double files are connected through P_2O_7 groups as in the diphosphate bronzes. Consequently this framework delimits square tunnels and diamond-shaped tunnels as in phosphate tungsten bronzes. It must also be pointed out that the vanadium ion is off centered in its octahedron so that it is more exactly characterized by a pyramidal coordination.

4. Mixed frameworks involving silicophosphate groups (Hagman and Kierkegaard 1968; Goodenough *et al* 1976; Leclaire *et al* 1984, 1985a, 1986)

The possibility of associating SiO_4 and PO_4 tetrahedra to MO_6 octahedra in order to build a three-dimensional framework characterized by tunnels is not obvious if one

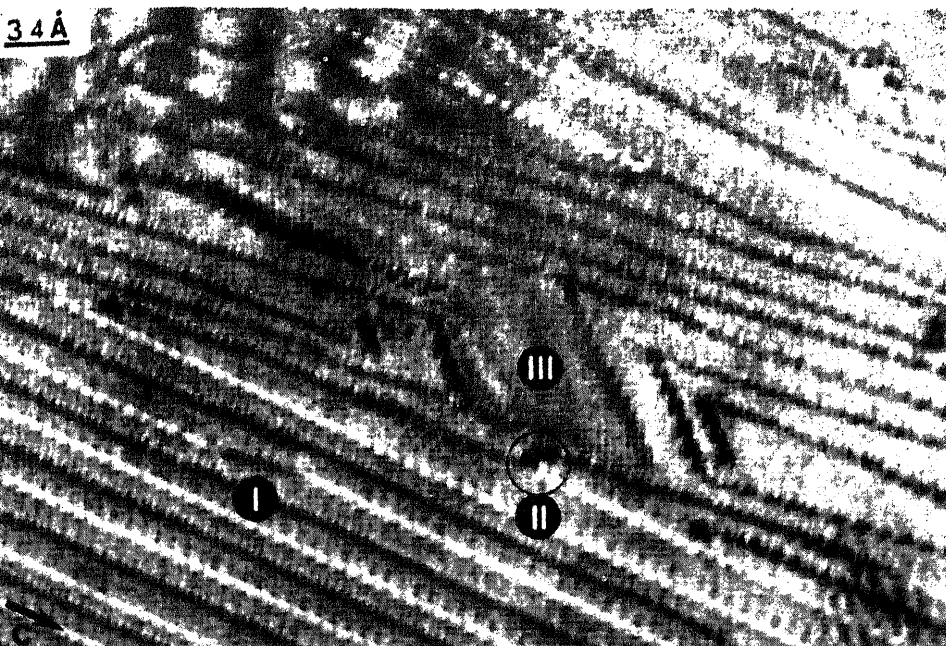


Figure 20. Complex association of diphosphate planes and crystallographic shear planes: detail of an HREM micrograph taken from a crystal $K(P_2O_4)_2(WO_3)_{2m}$ with $m = 38$. Zones I and II illustrate different types of interactions between diphosphate planes and shear planes. Zone III shows a hair-pin like contrast.

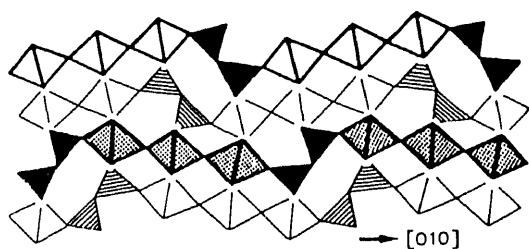


Figure 21. Structure of the oxide $P_8W_{12}O_{52}$.

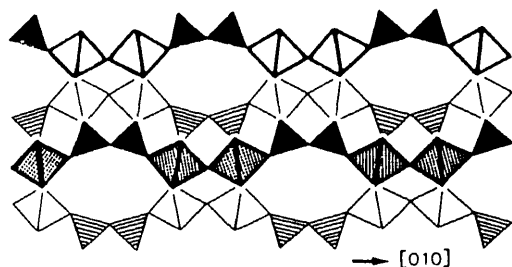


Figure 22. Structure of the bronze $CsP_8W_8O_{40}$.

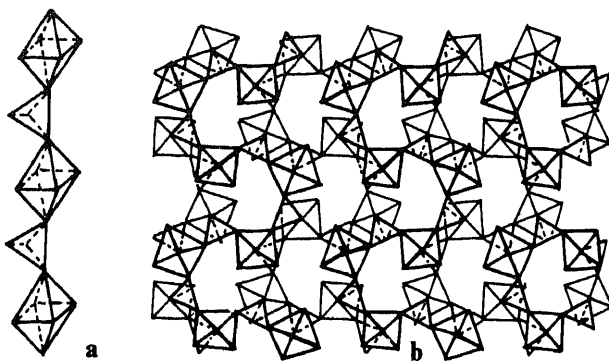


Figure 23. NaPWO_6 . (a) The infinite chains built up from WO_6 octahedra and PO_4 tetrahedra. (b) Lateral connection between the mixed chains forming an octahedral arrangement.

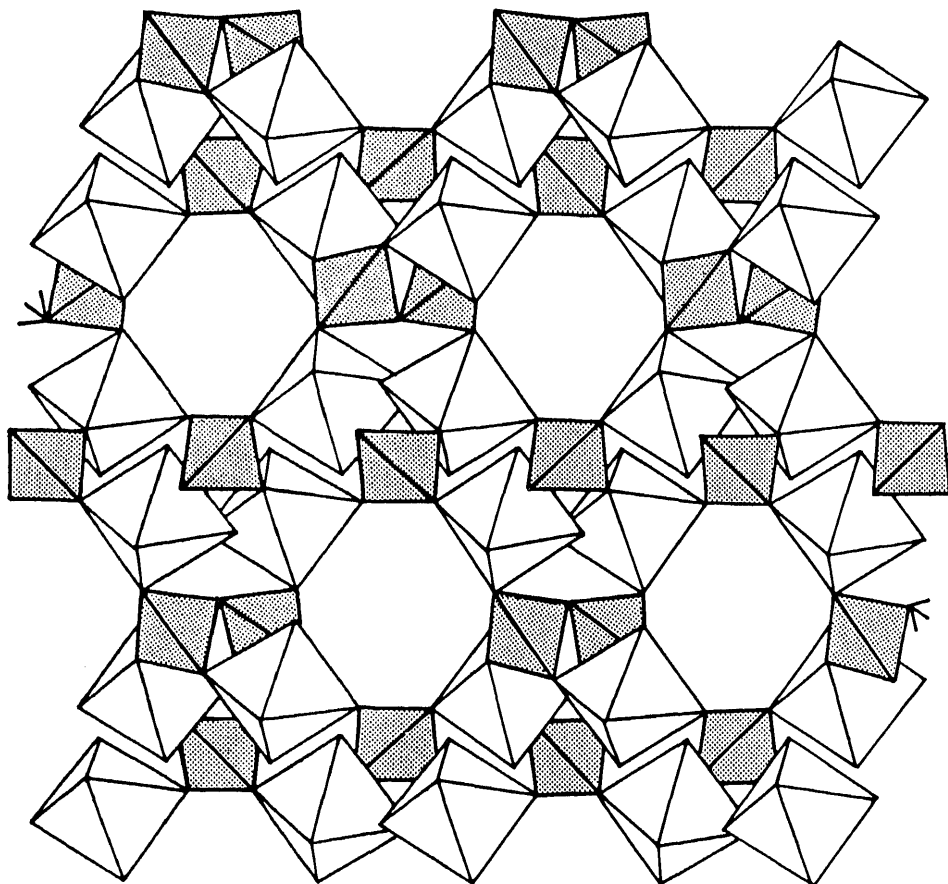


Figure 24. The host lattice of the molybdenophosphate $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$.

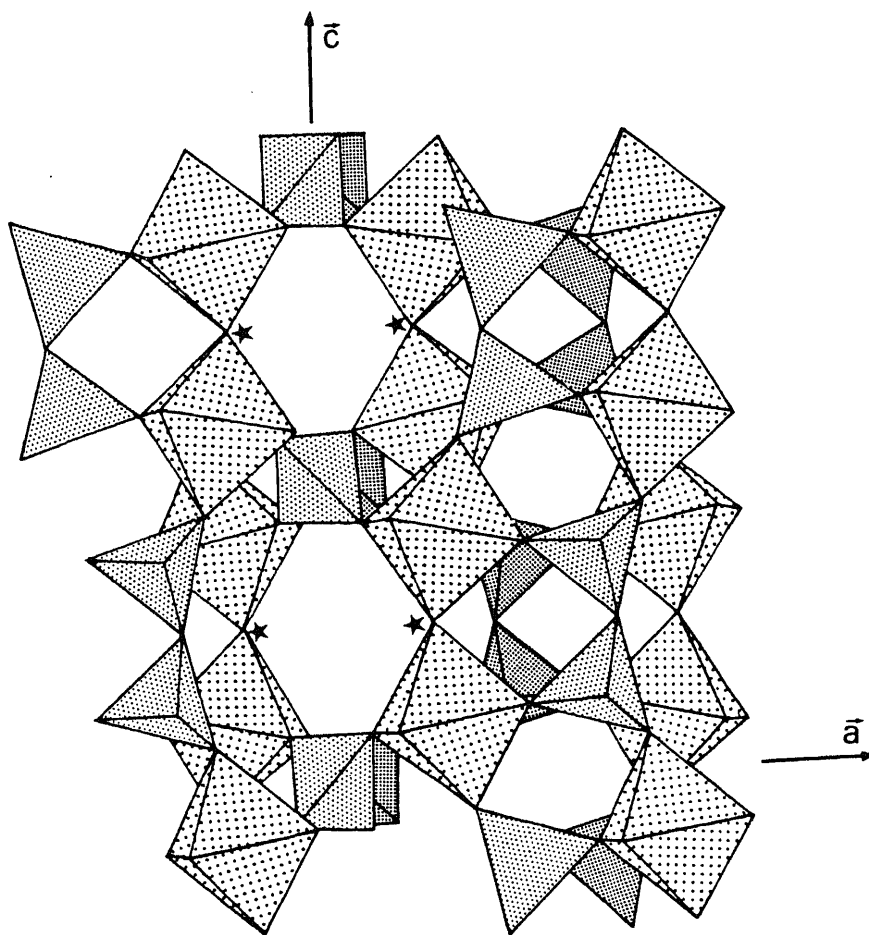


Figure 25. The host lattice of the molybdenum phosphate $\text{TiMo}_2\text{P}_3\text{O}_{12}$.

takes into account the great rigidity of the SiO_4 and PO_4 tetrahedra. Three examples of such frameworks are given by the silicophosphates $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$, $\text{V}_3\text{P}_5\text{SiO}_{19}$ and $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$.

The hexagonal silicophosphates $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$ ($A = \text{K, Rb, Tl, Cs}$; $M = \text{Mo, Ti, Sn}$) form a large family which is in fact represented by the oxide $\text{KM}_3\text{P}_5.8\text{Si}_2\text{O}_{25}$. The corner-sharing polyhedra which form the host-lattice of these oxides (figure 29) is characterized by tetrahedral units $\text{P}_6\text{Si}_2\text{O}_{25}$ which share their corners with MoO_6 octahedra. The tetrahedral units are built up of disilicate groups which share their corners with $2 \times 3 \text{ PO}_4$ tetrahedra. This three-dimensional network delimits tunnels running along the $[100]$ and $[110]$ directions. Consequently, these oxides are characterized by an intersecting tunnel structure and can exhibit ion exchange properties.

The hexagonal vanadosilicophosphate $\text{V}_3\text{P}_3\text{SiO}_{19}$ can be considered as a limiting case owing to the very small size of its tunnels as shown from the projection of its

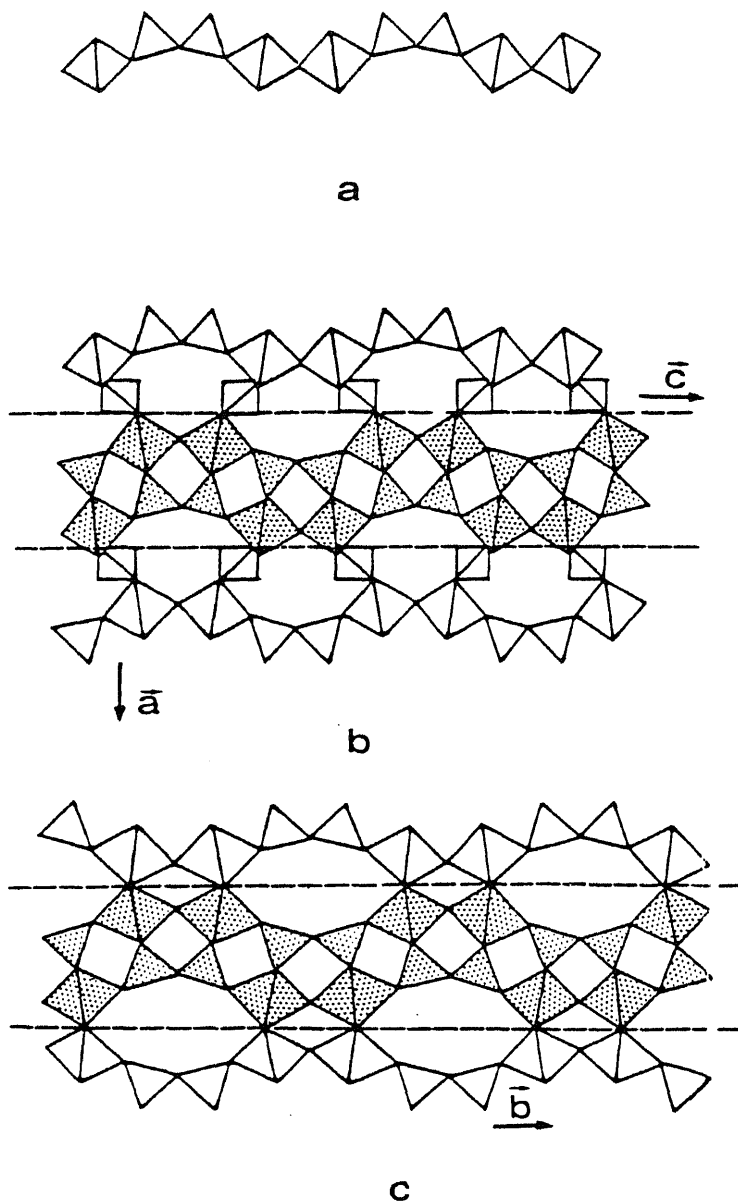


Figure 26. Comparison of the structure of the molybdenophosphate $\text{TiMo}_2\text{P}_3\text{O}_{12}$ with that of the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$. (a) The infinite chains built up from diphosphate groups and Mo_2O_{11} octahedral units. Relative dispositions and modes of connection of these chains (b) in the oxide $\text{TiMo}_2\text{P}_3\text{O}_{12}$ and (c) and in the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$.

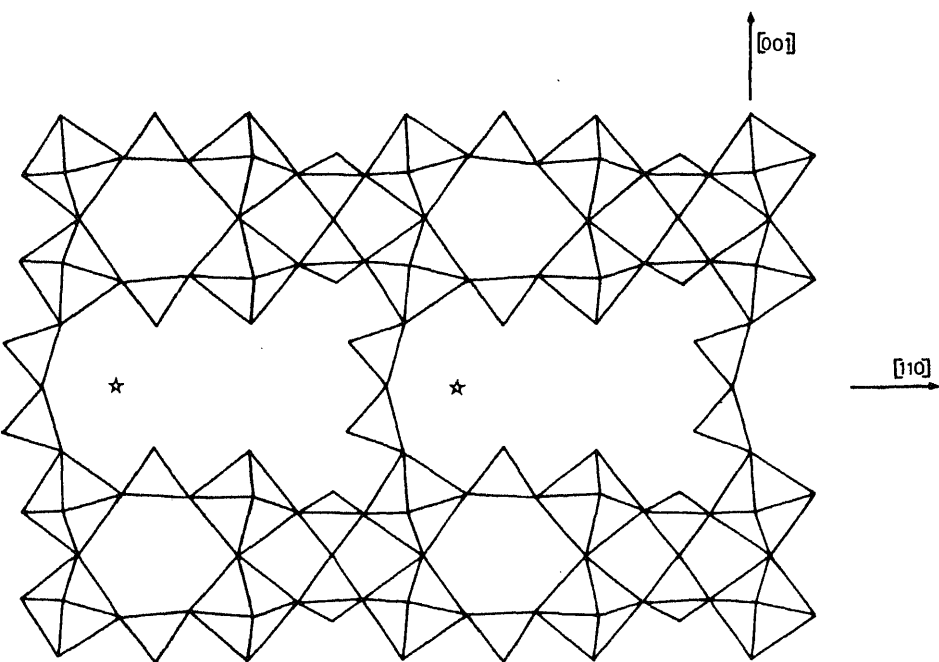
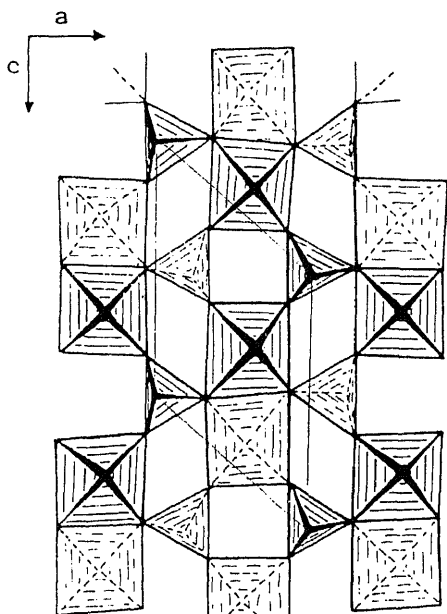


Figure 27. Similarity of $\text{TiMo}_2\text{P}_3\text{O}_{12}$ with the HTB structure: the framework is built up from the stacking of identical layers of the polyhedra forming hexagonal rings.



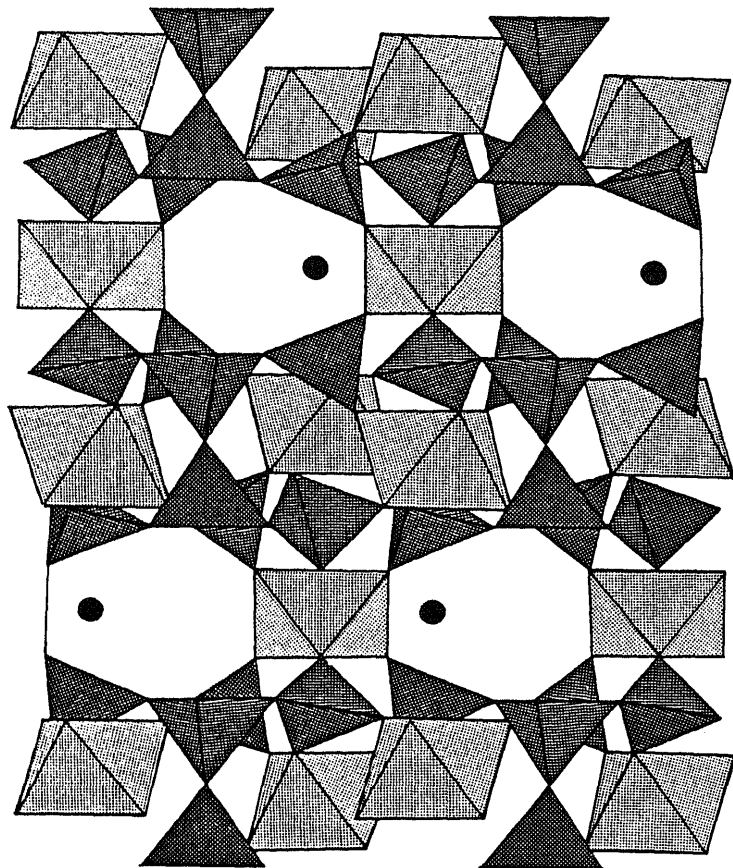


Figure 29. The host lattice of the hexagonal silicophosphate $KM_3P_6Si_2O_{25}$.

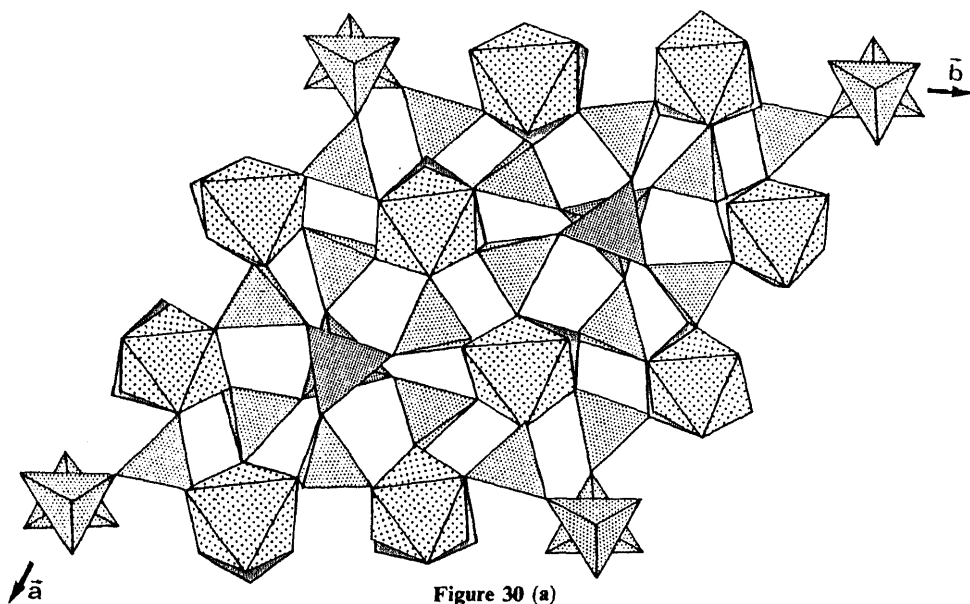
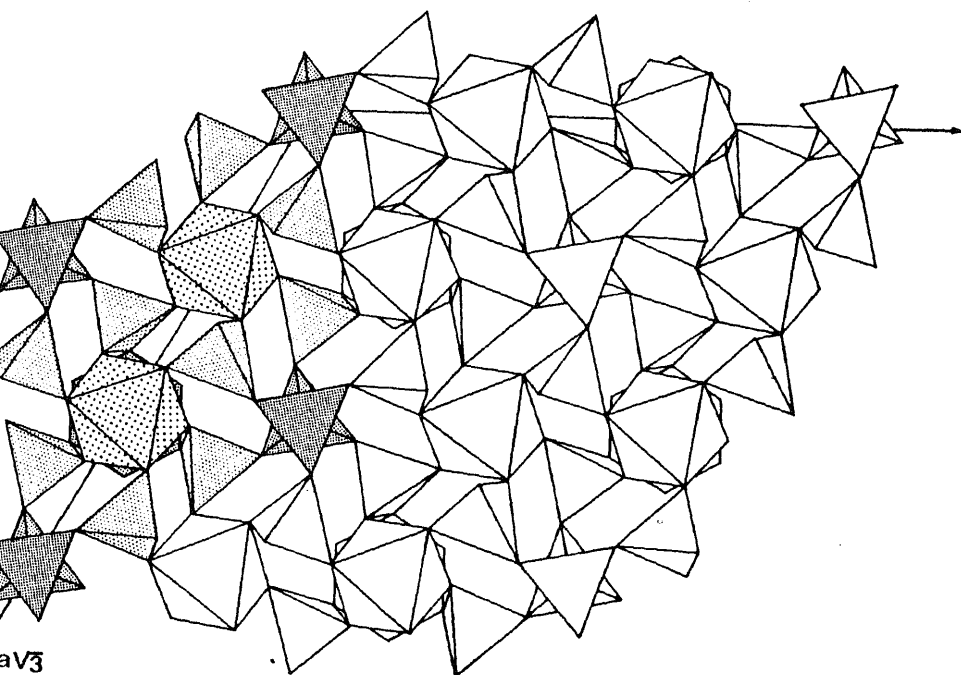
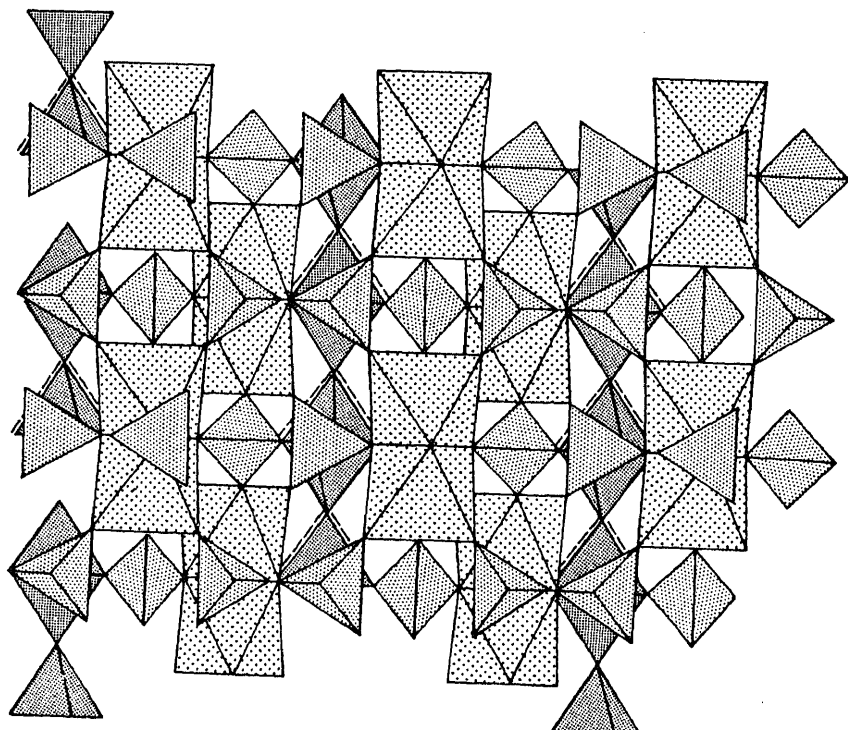


Figure 30 (a)



aV3

b



corner-sharing tetrahedra. The three-dimensional view of this structure (figure 30c) shows another particularity of this structure: the presence of octahedral clusters composed of two face-sharing octahedra; these clusters form infinite chains with the PO_4 tetrahedra extending along c , which can be compared to the strings $[\text{MoP}_2\text{O}_{15}]_3$ built up of three octahedra and six tetrahedra observed in the oxide $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$.

The silicophosphates $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ could be classified as phosphates as well as silicates since their homogeneity range extends from $x = 0$ to $x = 3$. In these compounds each ZrO_6 octahedron shares its six corners with SiO_4 and/or PO_4 tetrahedra, and each tetrahedron shares its four corners with four octahedra as shown in figure 31a. This mixed framework $\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ does not really form tunnels but large cavities (figure 31b) where the Na^+ ions are located; however these cavities communicate with one another so that Na^+ ions can move through the structure, involving superionic conductivity properties for these materials. It is worth noting that zirconium may be replaced by titanium or germanium.

5. Other examples of mixed frameworks of octahedra and tetrahedra (Lloyd *et al* 1976; Stone and Bursill 1977; Bursil 1979; Bursill and Stone 1981; Gasperin 1981; Agafonov 1985)

Besides the silicates, germanates and phosphates, few oxides with a mixed framework involving tetrahedra and octahedra are known, if one excepts the oxygen-deficient perovskites. The niobate, $\text{Cs}_2\text{Nb}_4\text{O}_{11}$, is an interesting example owing to the great size

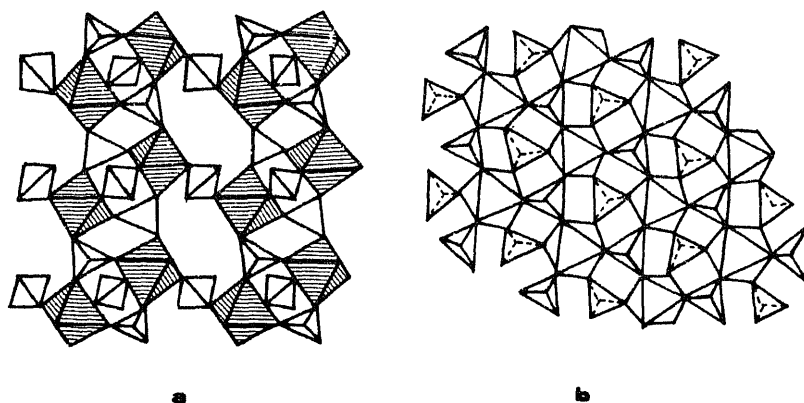


Figure 31. $\text{NaZr}_2(\text{PO}_4)_3$. (a) Three-dimensional view of the structure along the C_R direction of the rhombohedral cell. (b) Projection of half the unit cell along the a_R axis.

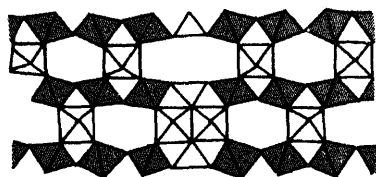


Figure 32. The host-lattice of the niobate $\text{Cs}_2\text{Nb}_4\text{O}_{11}$.

of its tunnels; the important family of oxides $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$ ($M = \text{Ti, Ge}$) is worth describing owing to its analogy with the shear structures and the DPTB.

The host-lattice of the niobate $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ (figure 32) is mainly built up of corner and edge-sharing octahedra; however a small number of NbO_4 tetrahedra participate in the structure. A striking similarity with the pyrochlore framework is observed as shown from the hexagonal tunnels running in different directions. The main difference with pyrochlores concerns the groups of two edge-sharing octahedra and their association with NbO_4 tetrahedra leading to the formation of wide tunnels where the Cs^+ ions are located; these tunnels can be compared to those observed in $\text{CsP}_8\text{W}_8\text{O}_{40}$ and $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$. Like the pyrochlores this oxide is characterized by a true intersecting tunnel structure which should exhibit ion exchange properties.

The structure of $\beta\text{-Ga}_2\text{O}_3$ which exhibits an anionic close-packing can also be considered as the limiting case of a tunnel structure: its framework (figure 33a) which is built up from structural units of Ga_4O_{24} formed of two GaO_4 tetrahedra and two edge-sharing GaO_6 octahedra, delimits diamond shaped tunnels. These latter are very similar to those of the hypothetical structure MO_2 (figure 33b) obtained by a simple tilting of the octahedra in the MO_2 rutile form (figure 33c). The close relationships between the two structures, rutile and $\beta\text{-Ga}_2\text{O}_3$, are confirmed by the ability of the Ga_4O_{24} units to fit the rutile framework. Ga_4O_{24} units can be introduced into the TiO_2 framework in the form of rows forming hexagonal tunnels which are empty. These rows delimit rutile slabs which are n octahedra wide; thus a large family, $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$, can be predicted in which n is an odd number which characterizes the number of octahedra corresponding to the width of the rutile slab; Ga_4GeO_8 , α , $\text{Ga}_4\text{Ge}_3\text{O}_{12}$, $\text{Ga}_4\text{Ti}_5\text{O}_{16}$ correspond to the first, second and third members of this series whereas the oxide $\text{Ga}_4\text{Ti}_{21}\text{O}_{48}$ represents the member $m = 21$ (figure 34a, b, c). The similarity of this structural family with the shear structures and with the diphosphate tungsten bronzes must be pointed out: the ' $[\text{Ga}_4\text{O}_6]_\infty$ planes' correspond to the 'phosphate planes' or to the shear planes whereas the rutile slabs can be replaced by ReO_3 -type slabs in the DPTB. It is worth noting that the geometry of the ' Ga_4O_{24} ' units does not allow the obtaining of an even number of octahedra for the rutile slabs; nevertheless the possibility of existence of even- n members resulting from the intergrowth of two odd- m members can be considered as shown for the hypothetical member $m = 4$ (figure 34d). The particular behaviour of the first member Ga_4GeO_8 , α is also remarkable: the ' Ga_4O_{24} ' units share their corners in

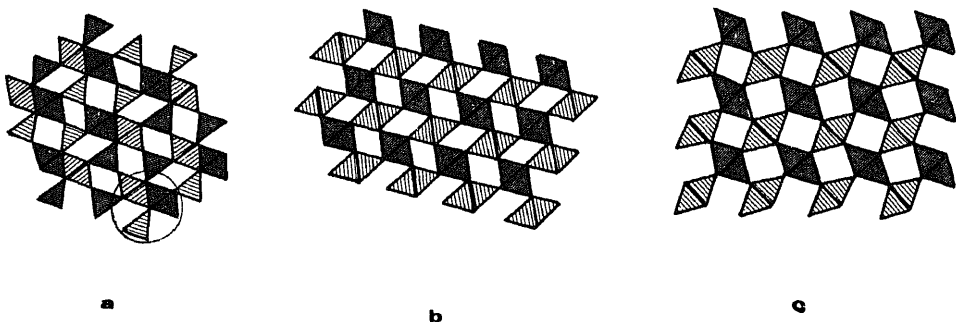


Figure 33. Comparison of (a) the $\beta\text{-Ga}_2\text{O}_3$ structure with (b) the hypothetical MO_2 oxide derived from (c) the rutile TiO_2 framework by tilting of the octahedra. One Ga_4O_{24} unit is circled.

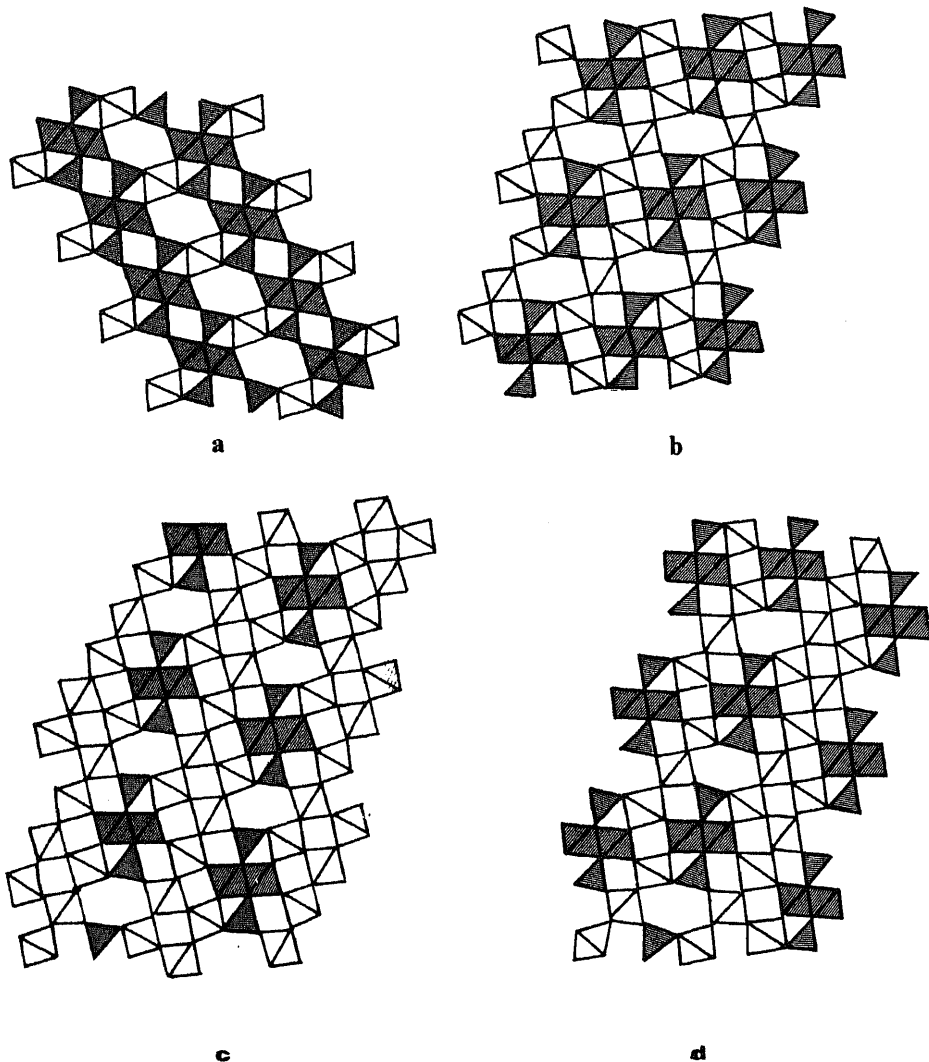


Figure 34. The three first odd members of the series $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$ (a) $n = 1$, (b) $n = 3$ and (c) $n = 5$ and (d) the hypothetical even- m member $m = 4$ corresponding to the intergrowth of the members $n = 3$ and $n = 5$. The Ga_4O_6 units are hatched.

one direction forming ' $\beta\text{-Ga}_2\text{O}_3$ '-type ribbons, so that an intergrowth between this oxide and $\beta\text{-Ga}_2\text{O}_3$ could be considered.

6. Conclusion

Oxides with a three-dimensional mixed framework built up from octahedra and tetrahedra correspond to a rather recent field of investigation which seems rather promising. The adaptability of phosphate groups to an octahedral framework, especially to WO_6 and MoO_6 octahedra is remarkable, such structural properties

should be used to induce a strong anisotropy in the metallic properties of those bronzes leading either to bidimensional conductors as in DPTB and MPTB or to unidimensional conductors as in $\text{CsP}_8\text{W}_8\text{O}_{40}$. The possibility of SiO_4 and GeO_4 tetrahedra forming a mixed framework seems more limited, owing to their great rigidity, nevertheless they show a good ability to connect with NbO_6 or TaO_6 octahedra. The investigation of mixed frameworks involving 'silicophosphates' groups is quite new, but the formation of an intersecting tunnel structure makes us think that it could be the starting point of the synthesis of tunnel structures intermediate between the octahedral frameworks and the tetrahedral zeolites. Gallium, is characterized by its tendency to form mixed frameworks owing to its ability to take up both octahedral and tetrahedral coordinations; moreover oxides such as $\text{Ga}_4\text{O}_6(\text{TiO}_2)_n$ are potential candidates for intercalation of small ions like Li^+ or Na^+ .

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Synthesis and structure of some interesting oxides of bismuth†

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Abstract. Synthesis and structures of several new oxides containing bismuth are described. Three types of structures are common among the multinary oxides containing trivalent bismuth. They are the sillenite structure of $\gamma\text{-Bi}_2\text{O}_3$, the layered perovskite structure of Aurivillius phases and the pyrochlore structure. The influence of Bi^{3+} : $6s^2$ lone pair electrons is seen in all the three structures. In transition metal oxides containing trivalent bismuth, d^0 cations (Ti^{4+} , Nb^{5+} , W^{6+}) stabilize the layered perovskite structure, while cations containing partially-filled d orbitals (V^{4+} , Cr^{3+} , Fe^{3+}) favour pyrochlore-related structures. Ferroelectric distortion of MO_6 octahedra of the d^0 cations seems to play an important role in stabilizing layered perovskite structures.

Keywords. Bismuth oxides; synthesis; structures; sillenites; Aurivillius (layered perovskite) phases; pyrochlores.

1. Introduction

Solid compounds containing bismuth, particularly the oxides, exhibit a rich structural chemistry. Besides the binary oxide, Bi_2O_3 , bismuth forms a large number of multinary oxides where the formal oxidation state of the element is either $3+$ or $5+$. Although the radius of Bi^{3+} (1.16 Å in VIII coordination) is comparable to that of La^{3+} (1.17 Å in VIII coordination), there is little structural similarity between the solid compounds of Bi^{3+} and La^{3+} (Wells 1974). In many of the bismuth compounds, the coordination around the metal is unsymmetrical, all the anions being bonded to one side of the cation. Typical examples of unsymmetrical coordination around Bi^{3+} in some of its oxides are shown in figure 1. The unique structural chemistry of Bi^{3+} oxides can be traced to the presence of stereoactive $6s^2$ lone pair electrons on the cation.

The influence of s^2 lone pair electrons on the structural chemistry of lone pair cations such as Bi^{3+} , Sb^{3+} , Pb^{2+} and Tl^+ has been discussed in the literature. Following the early attempts of Sidgwick and Powell (1940) and Gillespie and Nyholm (1957), who introduced the valence shell electron pair repulsion theory to rationalize the geometries of molecules containing lone pair atoms, Orgel (1959) invoked hybridization of the outer $6s$ and $6p$ orbitals to explain the observed stereochemistries of lone pair cations. Typically, in compounds of Tl^+ , Pb^{2+} and Bi^{3+} , the $6s$ orbital mixes with the empty $6p$ orbitals which are separated by ~ 6 eV, the lone pair taking up one of the hybridized $6s$ - $6p$ orbitals and the anions being bonded to the remaining orbitals. Together with the

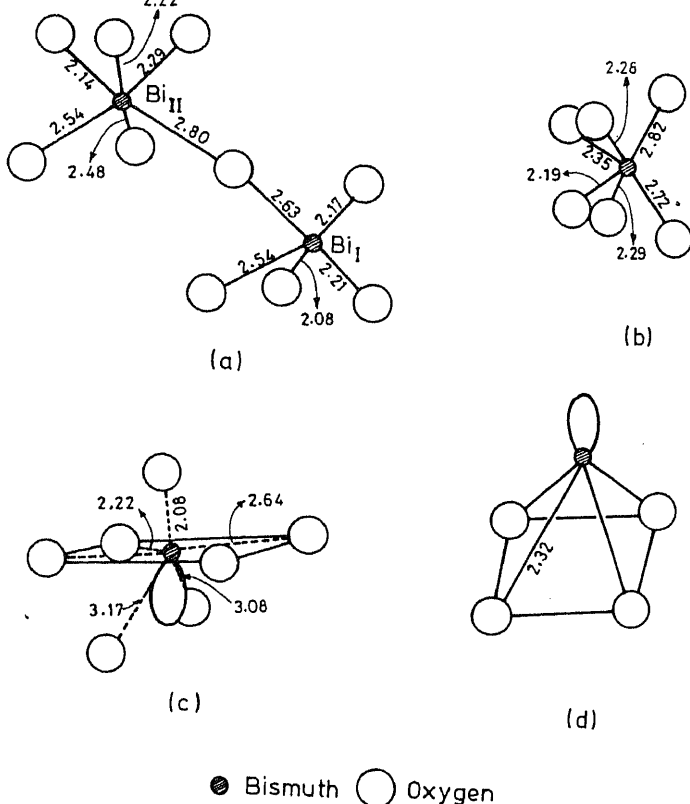


Figure 1. Coordination polyhedra around Bi^{3+} in some bismuth oxides showing the influence of the $6s^2$ lone pair. (a) $\alpha\text{-Bi}_2\text{O}_3$, (b) BiRe_2O_6 , (c) $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$ and (d) layered perovskites, e.g. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Andersson and Åström (1972) have pointed out that the lone pair electrons indeed take up a volume comparable to that of an anion in solids where the lone pair is stereoactive.

Unlike Bi^{3+} , Bi^{5+} adopts symmetrical (octahedral) coordination in its solid compounds. Bi^{5+} however is an unstable oxidation state being stabilized in fluorides and in some ternary oxides containing electropositive alkali or alkaline-earth metals.

There is considerable current interest in the oxides of bismuth in view of the interesting structures and properties exhibited by them (see, for example, Watanabe 1984, Tsubaki and Koto 1984). The present paper describes some of the work carried out in this laboratory on the synthesis and structures of novel metal oxides containing bismuth. The oxides investigated belong mainly to the sillenite family related to $\gamma\text{-Bi}_2\text{O}_3$ (Aurivillius and Sillén 1945), the Aurivillius family of layered perovskites containing (Bi_2O_2) layers (Aurivillius 1949) and the pyrochlore family. In several of these oxides, influence of the $6s^2$ lone pair on the structure is seen.

2. Experimental

Oxides containing bismuth and one or more of the following transition metals, Ti, V, Nb, W, Cr, Fe or lanthanide, were prepared. Preparations were carried out by the

conventional ceramic method as well as by low-temperature methods. A low-temperature 'wet' method involving reaction in a high alkaline medium was employed for the preparation of sillenite phases in the Bi-*M*-O (*M* = Mn, Fe, Co) systems (Ramanan and Gopalakrishnan 1985). Oxides of the general formula, $\text{Bi}_{2-x}\text{M}_x\text{WO}_6$ (*M* = Cr, Fe) were prepared from aqueous solutions of the component metal nitrates and ammonium tungstate (Ramanan *et al* 1983). Structural characterization of the oxides prepared were made by powder x-ray diffraction, electron diffraction, IR absorption spectroscopy and magnetic susceptibility measurements. The details are given elsewhere (Ramanan 1984).

3. Results and discussion

3.1 Sillenite phases

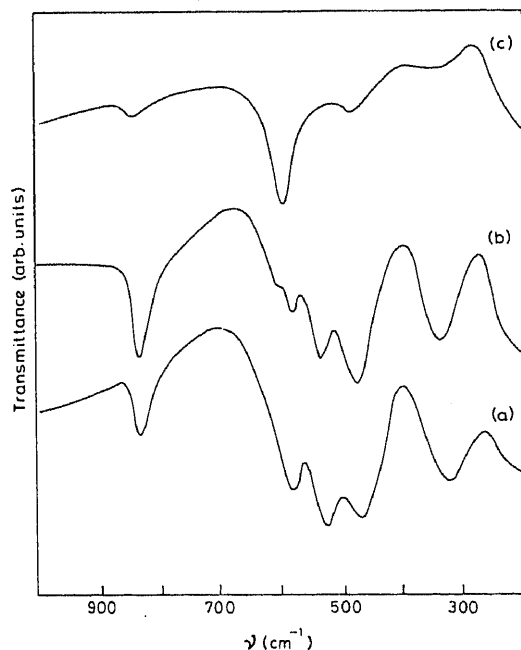
Ternary bismuth oxides related to $\gamma\text{-Bi}_2\text{O}_3$ possessing the general formula, $\text{Bi}_{26-x}\text{M}_x\text{O}_{40-y}$, where *M* = Si, Ge, Sn, Ti and $x = 2$ or *M* = Fe, Zn etc., and $x < 2$ are known as sillenite phases (Aurivillius and Sillén 1945; Levin and Roth 1964). They adopt a BCC structure (space group *I*23) with $a \approx 10.20 \text{ \AA}$. In this structure, Bi^{3+} has an unusual (5+2) oxygen coordination (figure 1) clearly revealing the influence of the $\text{Bi}^{3+}:6s^2$ lone pair on the structure (Abrahams *et al* 1967). The bismuth-oxygen polyhedra share corners and edges to form a $\text{Bi}_{24}\text{O}_{40}$ cluster. Although it is generally believed that the ternary *M* atoms in this structure occupy the tetrahedral 2(*a*) sites, as for example in the ideal cases of $\text{Bi}_{24}\text{Si}_2\text{O}_{40}$ and $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$, the concentration of *M* atoms in a number of sillenite phases is far in excess of the ideal composition. For instance, cubic phases of approximate composition BiMO_3 (*M* = Al, Co, Ni) have been reported in the literature (Tomashpol'skii *et al* 1969; Bucci 1971), but the details of their structures are not known. It is possible that such systems adopt sillenite structure where part of bismuth in the $\text{Bi}_{24}\text{O}_{40}$ cluster is substituted by *M* atoms.

Our investigations of sillenite phases in the $\text{Bi}_2\text{O}_3\text{-MO}_x$ (*M* = Mg, Al, Mn, Fe, Co and Ni) systems (Ramanan *et al* 1981; Ramanan and Gopalakrishnan 1985) have revealed that two kinds of sillenite phases are formed in many of these systems. One is the bismuth-rich phase which corresponds to the normal sillenite structure and the other is an *M*-rich phase which is formed especially when the preparation is carried out by a low-temperature method. As a typical case, in the Bi-Co-O system, we prepared two sillenite phases, $\text{Bi}_{25}\text{CoO}_{40}$ and $\text{Bi}_{10}\text{Co}_{16}\text{O}_{38}$. The former corresponds to the normal sillenite phase and its structure (BCC, $a = 10.11 \text{ \AA}$) and magnetic susceptibility ($\mu_{\text{eff}} = 5.00 \text{ BM}$, Co^{3+} (*S* = 2) at the tetrahedral site) are similar to those of $\text{Bi}_{25}\text{CoO}_{40}$ prepared by the high temperature method (Devallette *et al* 1982). The cobalt-rich phase, $\text{Bi}_{10}\text{Co}_{16}\text{O}_{38}$, also possesses the sillenite structure with nearly identical lattice parameter. The phase is formulated as $(\text{Co}^{2+})_2[\text{Bi}_{10}^{3+}\text{Co}_{14}^{3+}]\text{O}_{38}$ indicating that a substantial portion of bismuth in the $\text{Bi}_{24}\text{O}_{40}$ cluster of the sillenite structure is replaced by trivalent cobalt. Structural evidence that this formulation is most likely to be correct is provided by a refinement of x-ray powder diffraction intensities (table 1) on the basis of this model. The x-ray absorption spectrum of the cobalt-rich phase

Table 1. Refinement of x-ray powder diffraction intensities of $(\text{Co}^{2+})_2 [\text{Bi}_{10}^{3+} \text{Co}_{14}^{3+}] \text{O}_{38}$ in the sillenite structure.

<i>hkl</i>	<i>I</i> (obs)	<i>I</i> (calc) ^(a)	<i>hkl</i>	<i>I</i> (obs)	<i>I</i> (calc) ^(a)
220	2	6	611	30	34
310	100	92	532		
222	30	32	631	12	19
321	90	96	710		
400	11	12	550	14	20
411	12	15	543		
330			721	6	7
420	8	6	552		
332	5	2	633	4	8
422	25	27	651		
431	35	44	732	0	5
510			741		
521	6	10	811	12	12
530	21	24	554		
433			653	10	11
600	15	20	660		
442			822		

^(a) Intensities were calculated assuming that the structure is similar to $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$. The refined positional parameters are (2 Co) (2*a*), 0, 0, 0; (10Bi + 14 Co) (24*f*), 0.826 (4), 0.684 (1), 0.991 (2); O (1) (24*f*), 0.856 (21), 0.761 (16), 0.519 (15); O (2) (8*c*), 0.811 (15), 0.811 (15), 0.811 (15); O (3) (8*c*), 0.093 (8), 0.093 (8), 0.093 (8). The occupancy factor for oxygen is (38/40). $R_w = 15\%$.

**Figure 2.** Infrared absorption spectra of sillenite phases. (a) $\text{Bi}_{25}\text{FeO}_{40}$, (b) $\text{Bi}_{25}\text{CoO}_{40}$ and

seen in $\text{Bi}_{25}\text{CoO}_{40}$ and $\text{Bi}_{25}\text{FeO}_{40}$. In the cobalt-rich phase, a new band at 575 cm^{-1} , which may be due to $(\text{Co}^{2+}\text{O}_4)$ tetrahedra, appears while the strong band at 820 cm^{-1} disappears. Other changes in the spectrum are consistent with the substitution of part of the bismuth in the $\text{Bi}_{24}\text{O}_{40}$ cluster by Co^{3+} ions. The present investigation thus reveals the existence of a new type of sillenite phase wherein part of the bismuth at the (24f) sites of the sillenite structure are substituted by transition metal ions such as Co^{3+} and Fe^{3+} .

2. Aurivillius phases

Layered perovskite oxides of bismuth of the general formula, $(\text{Bi}_2\text{O}_2)^{2+} [A_{n-1}B_n\text{O}_{3n+1}]^{2-}$, where A is a large cation like Ba, Pb, Sr, Ca, Bi, K and Na and B is a smaller cation such as Ti, Nb, W, Fe etc., stable in octahedral coordination, are known as Aurivillius phases (Aurivillius 1949). These solids adopt a layered structure consisting of alternating PbO -like (Bi_2O_2) layers and $[A_{n-1}B_n\text{O}_{3n+1}]$ perovskite slabs (figure 3). They crystallize in orthorhombic (pseudotetragonal) structures with $a \simeq b \simeq 5.4\text{ \AA}$; the length of the c -axis varies with the thickness of the perovskite slab (n -value) (Newnham *et al* 1971; Hutchison *et al* 1977). We have prepared a number of new Aurivillius phases and examined their structures using x-ray and electron diffraction as well as electron microscopy (Gopalakrishnan *et al* 1984). The investigations have revealed a number of interesting features which are briefly presented here.

In the Bi_2O_3 - WO_3 system, we visualized the existence of a new homologous series, $\text{Bi}_2\text{W}_n\text{O}_{3n+3}$, as a special case of the more general Aurivillius family, where the perovskite component of the latter is replaced by a WO_3 component of corner-sharing WO_6 octahedra (figure 4). The two known phases in the system, Bi_2WO_6 and $\text{Bi}_2\text{W}_2\text{O}_9$ (Watanabe and Goto 1978), may be regarded as $n = 1$ and $n = 2$ members of this family. We have obtained evidence for the existence of the $n = 3$ member of this family by high resolution electron microscopic investigations of nominal $n = 3$ compositions (Jefferson *et al* 1982). The $n = 3$ member exists as a disordered intergrowth together with the more stable $n = 1$ and $n = 2$ members of this family. More importantly, we have synthesized a new family of ordered (recurrent) intergrowth phases of the general formula, $\text{Bi}_4A_{m+n-2}B_{m+n}\text{O}_{3(m+n)+6}$, which are formed between n and $n + 1$ ($= m$) members of the Aurivillius family (figure 5) (Gopalakrishnan *et al* 1984). The unit cell parameters of the new members of this series as derived from the x-ray and electron diffraction data are given in table 2. Lattice image of a typical member of this series is shown in figure 6. Although some members of this family were reported as isolated instances (Horiuchi *et al* 1977), our investigations have revealed the existence of a new homologous series of oxides based on ordered intergrowth of members of the Aurivillius family of oxides. A particularly interesting member of this homologous series is $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ which is formed by intergrowth of $n = 1$ and $n = 2$ -like units of the Aurivillius family. It is to be noted that the individual $n = 1$ and $n = 2$ members do not exist in this system. Formation of intergrowth phases in this family seems to have its origin in the minimization of elastic strain energy when the intergrowth occurs between the constituent units (Kikuchi 1979; Gopalakrishnan *et al* 1984; Jefferson *et al* 1984).

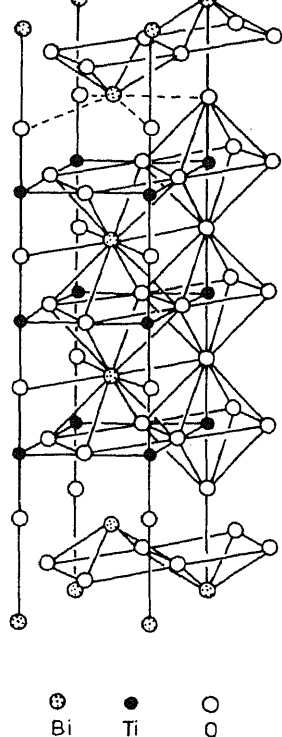


Figure 3. Idealised structure of an Aurivillius phase, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The distorted square antiprismatic coordination around Bi^{3+} in (Bi_2O_2) layer is indicated.

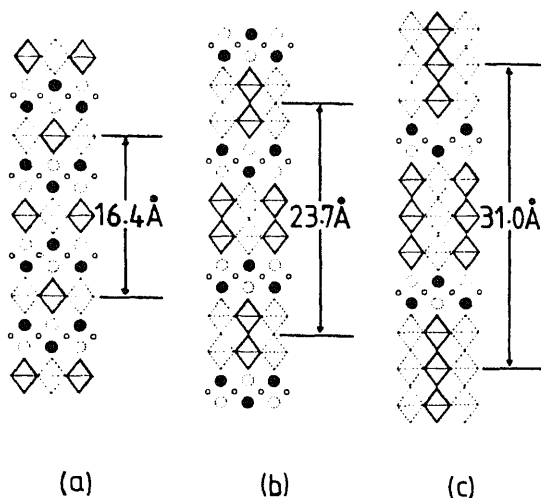


Figure 4. Idealised representations of the structures of $\text{Bi}_2\text{W}_n\text{O}_{3n+3}$ members. (a) Bi_2WO_6 , (b) $\text{Bi}_2\text{W}_2\text{O}_9$ and (c) $\text{Bi}_2\text{W}_3\text{O}_{12}$ (from Jefferson *et al* 1982).

forms additional weak bonds with the perovskite slabs which appear to be essential for the stability of the structure. In Bi_2WO_6 ($n = 1$ member), Bi^{3+} in the (Bi_2O_2) layer is coordinated to an additional oxygen of the WO_6 octahedron at a distance of 2.49 Å in such a way as to accommodate the $6s^2$ lone pair (Watanabe 1984). In the higher members of the Aurivillius family, each bismuth in the (Bi_2O_2) layer is surrounded by eight oxygen atoms, four from the layer and four more from the perovskite slab at longer distances, the coordination polyhedron around bismuth being a distorted square-antiprism (figure 3). That the Bi^{3+} : $6s^2$ lone pair plays a crucial role in the stability of Aurivillius phases is seen from the fact that the structure is destroyed by the substitution of other ions of similar size in the (Bi_2O_2) layer (Armstrong and Newnham 1972).

3.3 Pyrochlores

It is known that $6s^2$ lone-pair cations (Tl^+ , Pb^{2+} , Bi^{3+}) stabilize a defect-pyrochlore structure in a number of ternary oxides (Longo *et al* 1969). We have prepared two new oxides containing bismuth, BiCrWO_6 and BiFeWO_6 , that adopt a defect-pyrochlore

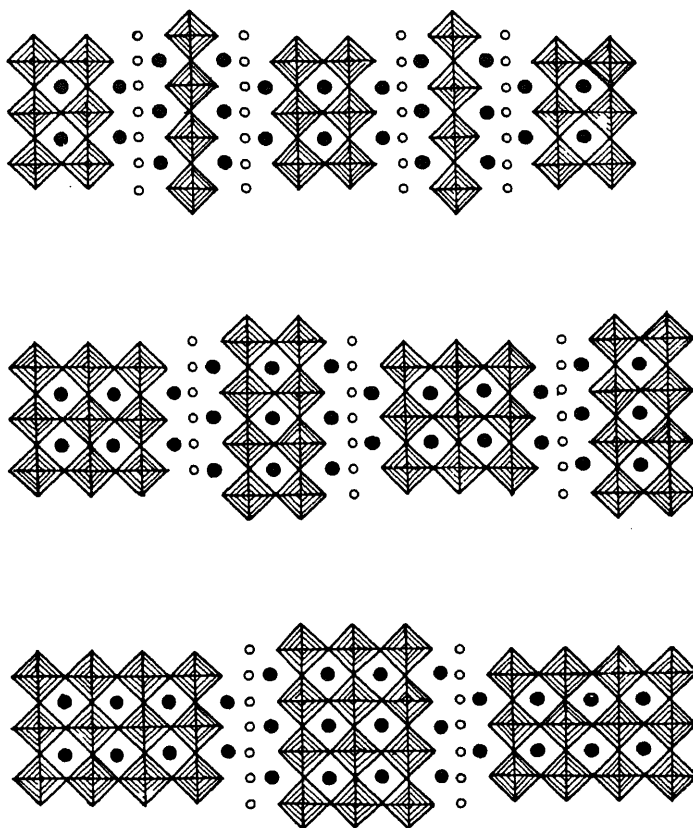


Figure 5. Idealised representations of the structures of intergrowth Aurivillius phases (from Gopalakrishnan *et al* 1984).

Table 2. Unit cell parameters of intergrowth Aurivillius phases

Compound	Perovskite layer sequence	Lattice parameters (Å)		
		<i>a</i>	<i>b</i>	<i>c</i>
$\text{Bi}_5\text{Nb}_3\text{O}_{15}$	1, 2	5.464	5.464	20.89
$\text{Bi}_7\text{Ti}_{4.5}\text{W}_{0.5}\text{O}_{21}$	2, 3	5.412	5.396	29.01
$\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$	3, 4	5.439	5.438	36.73
$\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$	3, 4	5.460	5.440	37.08
$\text{BaBi}_8\text{Ti}_7\text{O}_{27}$	3, 4	5.444	5.444	37.45
$\text{BaBi}_{12}\text{Ti}_{10}\text{O}_{39}$	3, 3, 4	5.428	5.428	53.68

structure (Ramanan *et al* 1983). The regular pyrochlore structure adopted by oxides of $\text{A}_2\text{B}_2\text{O}_7$ composition is cubic (space group $Fd3m$, $Z = 8$) where the large *A* cation occupies 8-coordinated (16*d*) sites and the smaller *B* cations take up octahedral (16*c*) sites (McCauley 1980; Subramanian *et al* 1983). For AB_2O_6 oxides crystallizing in the $Fd3m$ space group, two different structures are possible (Babel 1972): (i) a defect pyrochlore structure in which the (16*d*) sites are randomly occupied by eight *A* atoms

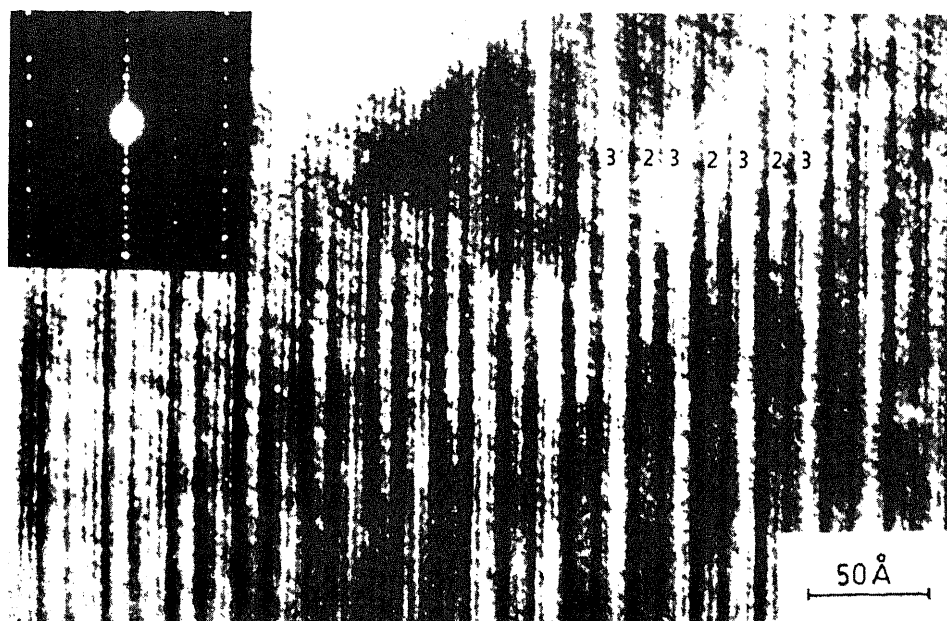


Figure 6. Lattice image of $\text{Bi}_7\text{Ti}_{4.5}\text{W}_{0.5}\text{O}_{21}$ showing ordered (recurrent) intergrowth of $n = 2$ and $n = 3$ members of the Aurivillius family. The corresponding electron diffraction pattern is shown. The electron beam is parallel to $[110]$.

and the $(8b)$ anion sites are vacant and (ii) the RbNiCrF_6 structure where the Rb atoms occupy the $(8b)$ sites leaving the $(16d)$ sites completely vacant. A refinement of x-ray powder diffraction intensities reveals that both BiCrWO_6 and BiFeWO_6 crystallize in a defect pyrochlore structure and not in the RbNiCrF_6 structure (Ramanan *et al* 1983). The defect pyrochlores are metastable having been formed because of the low temperature of synthesis. At high temperatures, they transform irreversibly to a tetragonal tungsten bronze structure with $a \simeq 12.40$ and $c \simeq 3.65$ Å.

More interestingly, we have obtained pyrochlore phases in several systems such as Bi-V-O, Bi-M-Cr-O and Bi-M-Fe-O ($M = \text{Nb}$ or Ta) whenever we have attempted to prepare layered perovskite (Aurivillius) phases (Ramanan *et al* 1985). Thus, the vanadium analogue of the layered perovskite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ cannot be prepared; instead attempts to prepare this phase by heating appropriate mixtures of Bi_2O_3 , V_2O_3 and V_2O_5 in sealed evacuated tubes resulted in the formation of a defect pyrochlore phase of composition $\text{Bi}_{1.33}\text{V}_2\text{O}_6$ which adopts an orthorhombic structure with $a = 7.04$, $b = 7.55$ and $c = 10.70$ Å. Similarly, attempts to prepare intergrowth Aurivillius phases (cf. §3.2) of composition $\text{Bi}_7\text{Nb}_3\text{Cr}_2\text{O}_{21}$ and $\text{Bi}_7\text{Nb}_3\text{Fe}_2\text{O}_{21}$, which would be isostructural with $\text{Bi}_7\text{Ti}_{4.5}\text{W}_{0.5}\text{O}_{21}$ (Gopalakrishnan *et al* 1984), have always resulted in pyrochlore phases $\text{Bi}_2\text{NbCrO}_7$ and $\text{Bi}_2\text{NbFeO}_7$. These results have led us to examine in general the relative stabilities of layered perovskite and pyrochlore structures in transition metal oxides containing bismuth (Ramanan *et al* 1985). It appears that d^0 cations stabilize the layered perovskite structure, while cations containing partially filled d orbitals (which suppress ferroelectric distortion of BO_6 octahedra) favour pyrochlore-related structures, the reason being that the formation of layered perovskite structure requires the presence of weak bonds between the (Bi_2O_2) layers

and the perovskite slabs, which entails considerable distortion of the BO_6 octahedra. This distortion is possible only with d^0 cations such as Ti^{4+} , Nb^{5+} or W^{6+} which are known to exhibit ferroelectric distortions of the perovskite structure (Goodenough and Longo 1970).

4 Other bismuth oxides

Metal oxides containing Bi^{5+} are relatively rare. Two interesting examples of Bi^{5+} -containing oxides are BaBiO_3 (Cox and Sleight 1979) and $\text{Sr}_2\text{Bi}_2\text{O}_7$ (Knop *et al* 1980). BaBiO_3 is a mixed-valence perovskite-related oxide containing both Bi^{3+} and Bi^{5+} , while $\text{Sr}_2\text{Bi}_2\text{O}_7$ containing exclusive Bi^{5+} adopts a weberite structure. We have attempted to synthesize similar oxides containing Bi^{5+} . We have been able to prepare weberite-related phases of the formula $\text{NaLnBi}_2\text{O}_{7-x}$ (Ln = La, Nd, Gd or Y; $x = 0.5$) by a low temperature method involving decomposition of metal nitrates (Ramanan and Gopalakrishnan 1982). The weberite-related phases lose oxygen around 750°C giving $\text{NaLnBi}_2\text{O}_6$ which crystallize in a monoclinic (ordered perovskite) structure. In both the structures, Bi^{5+} adopts a regular octahedral oxygen coordination as expected.

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Metal-hydrazine complexes as precursors to oxide materials

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Abstract. Metal-hydrazine complexes, $[M(N_2H_4)_n]^{2+}$ ($M = Mn, Fe, Co, Ni, Zn$ and Cd , $n = 2$ or 3) with different anions like sulphate, sulphite, acetate, formate, oxalate, hydrazinocarboxylate, nitrate and perchlorate have been investigated as precursors to oxide materials. The thermal reactivity of these complexes changes dramatically with the anion, e.g. sulphate, sulphite, acetate and formate complexes – decompose; oxalate and hydrazinocarboxylates – deflagrate and nitrate and perchlorate complexes – detonate. The deflagrating nature of the metal-hydrazine oxalates and hydrazinocarboxylates has been employed in the combustion synthesis of fine particle γ - Fe_2O_3 , Fe_3O_4 , ferrites and cobaltites at low temperature.

Keywords. Metal-hydrazine complexes; precursors to oxide materials.

1. Introduction

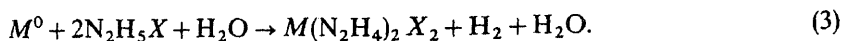
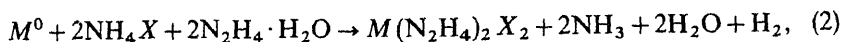
The chemistry of hydrazine is of interest since it has a potent N–N bond, two free electron pairs and four substitutable H-atoms. The coordination of hydrazine to the metal ion can either be as a unidentate or bridged bidentate ligand. Hydrazine has positive heat of formation ($\Delta H_f^\circ = \sim 12 \text{ kcal mol}^{-1}$) and therefore is thermodynamically unstable. Practically, however, it is quite stable and can be handled safely. Hydrazine is susceptible to catalysis and can explode even at room temperature in presence of rust (Fe_2O_3). Thermal reactivity of metal-hydrazine complexes is of interest since the stability of the complexes changes dramatically, depending upon the anion as well as the cation. In this paper, an attempt is made to correlate the reactivity of metal-hydrazine complexes, $[M(N_2H_4)_n]^{2+}$ ($M = Mn, Fe, Co, Ni, Zn$ and Cd , $n = 2$ or 3) as a function of anions like sulphate, sulphite, acetate, formate, oxalate, hydrazinocarboxylate, nitrate and perchlorate.

2. Experimental

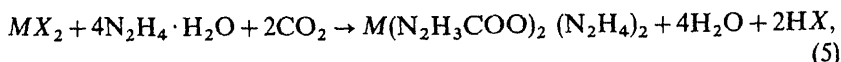
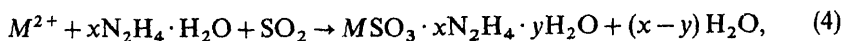
2.1 Preparation of metal-hydrazine complexes, $M(N_2H_4)_nX_2$

The general method of the preparation of metal hydrazine complexes, $M(N_2H_4)_nX_2$ ($M = Mn, Fe^*, Co, Ni, Zn$ and Cd , $n = 2$ or 3), and $X =$ acetate, oxalate, formate nitrate or sulphate) involves the reaction of an aqueous solution of the corresponding metal salt with alcoholic hydrazine hydrate

The complexes can also be prepared by dissolving the metal powders in a solution of ammonium (NH_4^+) or hydrazinium (N_2H_5^+) salts in hydrazine hydrate or water,



Metal sulphite and metal hydrazinocarboxylate hydrazine complexes were prepared by the reaction of aqueous metal ions with hydrazine hydrate saturated with SO_2 and CO_2 , respectively,



2.2 Analysis

The metal content in the complexes was determined by EDTA complexometric titrations. Hydrazine content was estimated volumetrically using 0.025 M KIO_3 solution under Andrews conditions (Vogel 1961).

2.3 Physicochemical studies

Infrared spectra of the complexes were recorded as nujol mulls or KBr discs using a Perkin-Elmer 781 spectrophotometer. Simultaneous TG-DTG-DTA of the complexes were recorded using a TGD-5000 RH thermobalance of ULVAC Sinku Riko, Japan. Thermal analysis curves were recorded in air using 4–5 mg samples. The heating rate employed was $10^\circ\text{C}/\text{min}$. Platinum cups were used as sample holders.

The decomposition/combustion residues of the complexes were characterized by x-ray powder diffraction patterns recorded on a Philips PW 1050/70 diffractometer using Cu K_α and Co K_α radiation.

Temperature profile measurements to determine the surface temperatures in the combustion of $\text{FeC}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ and $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ were carried out using chromel-alumel thermocouple embedded in 1 cm^3 pellets. A time-temperature plot was obtained by feeding the output to a strip-chart recorder.

BET surface area of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, ferrites and cobaltites were measured by nitrogen adsorption using Micromeritics Accusorb 2100 E instrument. Mossbauer spectra of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ were recorded at room temperature employing a ECIL MBS 35 spectrophotometer with a multichannel analyser. Coercivity of $\gamma\text{-Fe}_2\text{O}_3$ was measured using EG & G vibrating sample magnetometer fitted with bipolar power supply.

3. Results and discussion

Preparation, infrared spectra and thermal analysis of metal hydrazine complexes

al 1981; Govindarajan *et al* 1985), acetate (Mahesh and Patil 1985) and sulphite (Budkuley 1984) have been investigated.

The hydrazine molecule is coordinated to the metal as a bridged bidentate ligand in all these complexes except in the case of hydrazinocarboxylates in which it is coordinated to the metal atom as a unidentate ligand. Infrared spectra serve as a fingerprint technique and the presence of unidentate N_2H_4 in $M(N_2H_3COO)_2(N_2H_4)_2$ is indicated by the characteristic N-N stretching frequency of $N_2H_4 \sim 930\text{ cm}^{-1}$ (Nicholls and Swindells 1968). The x-ray crystal structure of $Zn(N_2H_3COO)_2(N_2H_4)_2$ has been determined and the structures of Mn, Fe, Co & Ni complexes are reported to be isomorphous (Ferrari *et al* 1966). This study supports the presence of unidentate N_2H_4 in these complexes.

The presence of bridged bidentate hydrazine in sulphate, sulphite, formate, acetate, nitrate and oxalate complexes has been indicated by the presence of ν_{N-N} of N_2H_4 in the region $960\text{--}980\text{ cm}^{-1}$ (Patil *et al* 1981, 1982a, b; Braibanti *et al* 1968) and x-ray crystal structure studies (Ferrari *et al* 1965).

Thermal reactivity of metal-hydrazine complexes has been investigated by TG-DTA studies. Table 1 summarizes the results of the thermal decomposition of metal sulphate, sulphite, formate and acetate hydrazine complexes. All these complexes initially lose hydrazine exothermically leaving behind the respective metal salts which decompose to the corresponding metal oxides at higher temperatures. The oxide formation temperatures are lower compared to those reported for hydrated metal salts. The metal salts formed by the dehydrazination of the complexes are reactive and decompose at lower temperatures.

Table 2 summarizes the results of TG-DTA studies of metal nitrate, oxalate and hydrazinocarboxylate hydrazine complexes. All these complexes show single step decomposition in TG giving corresponding metal oxides. The decomposition of nitrate complexes is violent. The oxalate and hydrazinocarboxylate complexes exhibit autocatalytic combustion behaviour, i.e., combustion is self-sustained once initiated.

Table 1. Thermogravimetric (temperature range °C) and differential thermal analysis* (peak temperature °C) data of metal hydrazine complexes $M(N_2H_4)_2X_2$.

Metal (M)	Anion (X)				Reaction
	Sulphate	Sulphite	Formate	Acetate	
Mn	175–245 (180)	202–295 (233)	110–178 (170-endo)	130–205 (150, 190)	Dehydrazination
Fe	100–250 (160)†	130–142 (135)†	—	—	Dehydrazination and Decomposition
Co	185–385 (200, 325)	150–160 (157)	100–204 (167-endo)	160–220 (180, 220)	Dehydrazination
Ni	230–485 (280, 455)	104–215 (182)	116–233 (217)†	190–245† (205, 230)	Dehydrazination
Zn	100–425 (110, 245, 350)	200–235 (215)	100–324 (168-endo)	150–195 (130)	Dehydrazination
Cd	155–385 (175, 330)	—	100–285 (187-endo)	115–215 (175, 200)	Dehydrazination

* All temperatures are within the range indicated by the endo and exo terms.

Table 2. Thermogravimetric (temperature range °C) and differential thermal analysis* (peak temperature °C) data of metal-hydrazine complexes, $M(N_2H_4)_nX_2$.

Metal <i>M</i>	Nitrate†	Oxalate	Anion (<i>X</i>)	Product
			Hydrazinocarboxylate	
Mn	(141)	204–225 (217)	130–290 (174, 195)	MnO
Fe	(140)	180–310 (202)	130–205 (135, 175)	Fe ₂ O ₃
Co	(188)	204–358 (209, 262)	210–269 (190, 200)	Co ₃ O ₄
Ni	(220)	226–419 (219, 244, 290)	187–200 (195, 228)	NiO
Zn	(212)	120–466 (216, 301, 406)	155–325 (200, 310)	ZnO
Cd	(145)	169–456 (182, 291, 353)	—	CdO

* All DTA peaks are exothermic; † $M(N_2H_4)_3(NO_3)_2$.

The decomposition/combustion of these complexes is accompanied by the evolution of large amounts of gases like NH_3 , H_2O , CO_2 and N_2 . The combustion residues thus left behind are fine and porous metal oxides.

Based on the thermal decomposition studies of metal-hydrazine complexes they can be classified into three distinct groups:

- 1) Complexes which decompose, i.e., lose hydrazine leaving behind corresponding metal salts. e.g. $M(N_2H_4)_2X_2$, where X = sulphate, sulphite, formate and acetate.
- 2) Complexes which deflagrate, i.e., exhibit self-sustained (controlled) combustion, e.g. $M(N_2H_4)_2C_2O_4$ and $M(N_2H_3COO)_2(N_2H_4)_2$.
- 3) Complexes which detonate, e.g. $M(N_2H_4)_3(NO_3)_2$ and $M(N_2H_4)_2(ClO_4)_2$.

This dramatic change in the reactivity of the metal-hydrazine complexes can thus be attributed to the nature of the anion i.e. inert, reducing or oxidising. The sulphate and acetate anions are quite inert and do not exhibit any deflagration or detonation. Whereas formate and sulphite complexes although lose hydrazine during decomposition, exhibit self-sustained combustion like oxalate and hydrazinocarboxylate complexes. The explosive nature of nitrate and perchlorate complexes can be attributed to the redox reactions of oxidizer-fuel groups in the complexes.

The role of cation (metal) is also quite important since the explosive nature of transition metal perchlorate hydrazine complexes (Friedrich and Vervoorst 1926; Maissen and Schwarzenbach 1951) changes to deflagration in the case of magnesium and aluminium perchlorate complexes (Patil *et al* 1982b). Thus, the highly unstable and explosive nature of N_2H_4 can be controlled by suitably complexing it with selective metal ions and anions.

4. Combustion synthesis

The deflagrating nature of metal oxalate and hydrazinocarboxylate hydrazine complexes has been employed in the combustion synthesis of fine particle Fe_3O_4 , γ - Fe_2O_3 , ferrites and cobaltites.

4.1 Synthesis of Fe_3O_4

The decomposition/combustion of $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$ in vacuum at $\approx 250^\circ\text{C}$ yields finely divided Fe_3O_4 . Formation of Fe_3O_4 was confirmed by x-ray powder diffraction pattern of the residue ($a = 8.46 \text{ \AA}$). The crystallite sizes of Fe_3O_4 calculated from x-ray line broadening are in the range of 170–250 $\text{\AA}$. The surface area of Fe_3O_4 is $50 \text{ m}^2/\text{g}$. The Mossbauer spectrum of Fe_3O_4 shows the expected hyperfine spectra with the central doublet indicating super paramagnetic nature of the particles. The DTA of this fine particle Fe_3O_4 shows two exotherms at 200°C and 630°C corresponding to the oxidation of $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ respectively.

4.2 Synthesis of $\gamma\text{-Fe}_2\text{O}_3$

The decomposition/combustion of $\text{FeC}_2\text{O}_4 (\text{N}_2\text{H}_4)_2$ in air at $\approx 200^\circ\text{C}$ yields a mixture of γ and $\alpha\text{-Fe}_2\text{O}_3$ as evidenced by the x-ray powder diffraction of the combustion residue. However, the decomposition/combustion of $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$ in air at $\approx 200^\circ\text{C}$ gave $\gamma\text{-Fe}_2\text{O}_3$ only as indicated by the XRD pattern of the combustion residue ($a = 8.37 \text{ \AA}$). The crystallite sizes of $\gamma\text{-Fe}_2\text{O}_3$ are in the range of 170–250 $\text{\AA}$ and the surface area is $40 \text{ m}^2/\text{g}$. Mossbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ showed the expected hyperfine split pattern. The hyperfine field calculated from the fitting of the spectrum is 490 kOe and the isomer shift is 0.3435 mm/sec with respect to stainless steel. The coercivity force observed from the B-H curve of $\gamma\text{-Fe}_2\text{O}_3$ is 170 oersteds. The DTA of $\gamma\text{-Fe}_2\text{O}_3$ showed an exotherm at $\approx 630^\circ\text{C}$ corresponding to the conversion of $\gamma \rightarrow \alpha\text{Fe}_2\text{O}_3$.

Temperature profile measurement of $\text{FeC}_2\text{O}_4 (\text{N}_2\text{H}_4)_2$ (Kishore *et al* 1986) showed that the maximum temperature attained during the combustion is $\approx 600^\circ\text{C}$ although ignition occurs at $\sim 200^\circ\text{C}$. On the other hand, in the case of $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$ combustion the maximum temperature attained was only 425°C . This difference in the exothermicity of the combustion of $\text{FeC}_2\text{O}_4 (\text{N}_2\text{H}_4)_2$ and $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$ is probably responsible for the formation of a mixture of γ , $\alpha\text{Fe}_2\text{O}_3$ in the former and exclusively $\gamma\text{-Fe}_2\text{O}_3$ in the latter. It is well known that $\gamma\text{-Fe}_2\text{O}_3$ is converted to $\alpha\text{-Fe}_2\text{O}_3$ at $\approx 600^\circ\text{C}$.

4.3 Synthesis of ferrites

The preparation of spinel ferrites by the decomposition/combustion of mixed metal oxalate hydrazinates, $M\text{Fe}_2 (\text{C}_2\text{O}_4)_3 (\text{N}_2\text{H}_4)_6$ where $M = \text{Mn, Fe, Co, Ni and Zn}$ at low temperatures has been reported (Gajapathy and Patil 1983).

Ultrafine ferrite powders have been prepared by the decomposition/combustion of solid solution precursors of the type $M_{1/3}\text{Fe}_{2/3} (\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$, where $M = \text{Mg, Mn, Co, Ni and Zn}$. These precursors decompose at lower temperatures ($125\text{--}150^\circ\text{C}$) with the evolution of large amounts of gases like NH_3 , H_2O , CO_2 and N_2 to yield corresponding ferrites. Formation of ferrites was confirmed by their characteristic x-ray patterns. The crystallite sizes of the ferrites calculated from their x-ray

$\text{MgCo}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{N}_2\text{H}_4$ and $\text{NiCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ has been reported (Patil *et al* 1983). The decomposition/combustion of solid solution precursors of the type, $\text{M}_{1/3}\text{Co}_{2/3}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$, where $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Ni}$ and Zn yield fine particle cobaltites, MCo_2O_4 at low temperatures (200–400°C). Further work is in progress on the characterization of these cobaltites.

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On the kinetics of crystal growth from a supercooled melt†

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Abstract. We present a theoretical analysis of the dynamics of crystal growth from a supercooled melt. A molecular theory of crystal growth that pays proper attention to the structure at the liquid-solid interface is discussed.

Keywords. Liquid-solid transition; crystal growth; supercooled melt; order parameters; diffusion equation; structure factor; heat mode.

1. Introduction

Kinetics of crystal growth has been a subject of absorbing interest for several decades (Cahn 1960; Cahn *et al* 1964; Bennema and Gilmer 1973; Carruthers 1979; Langer 1980). Recently attention has been focussed on understanding the dynamics of crystal growth from a microscopic basis. In this article we present a molecular theory of crystal growth developed by Bagchi and Kirkpatrick (1986) and discuss some of its consequences. In the next section we discuss the structure at the liquid-solid interface and its relevance to the kinetics of crystal growth. In §3 we describe the recent theory of Bagchi and Kirkpatrick. Section 4 concludes with a discussion.

2. Structure at the liquid-solid interface

Despite considerable effort over the years, the structure of the liquid-solid interface remains controversial and poorly understood. The main reason for this uncertainty is that it is difficult to obtain experimental information about the interface which is quite narrow and is bounded by two condensed phases. Most of our understanding on the structure of the interface comes from computer simulations (Cape and Woodcock 1980; Broughton *et al* 1981; Cleveland *et al* 1982) and from theoretical studies (Cahn and Kikuchi 1985; Haymet and Oxtoby 1981; Oxtoby and Haymet 1983; Tempkin 1966). Computer simulation studies indicate that the liquid-solid interface of a simple one-component system may be 6-8 monolayers wide. The decay of crystalline order may depend on the orientation of the crystalline solid. Theoretical investigations have reached similar conclusions on the structure of the interface. In the following we briefly discuss two theoretical studies that are relevant to the present work.

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The first study we discuss is that of Tempkin (1966) who proposed a multi-layer model of the interface. The merit of the Tempkin model is that it does not limit the number of layers and that it can be applied to different kinds of interfaces. This model consists of an infinite number of layers with the thickness d_{hkl} , the interplanar distance of the (hkl) face. Molecules in each layer are divided into solid-like and liquid-like molecules. A solid-like molecule can occur only on another solid molecule. The fraction of solid molecules in the n th layer, C_n , is the order parameter in this model. In the Tempkin model, n ranges from $-\infty$ (solid) to $+\infty$ (liquid) with $C_{-\infty} = 1$ and $C_{+\infty} = 0$. The assumption of solid on solid (sos) rules out 'overhangs' and implies that $C_{n+1} \leq C_n$. In the Tempkin formalism one calculates the change in Gibbs free energy that occurs if a completely flat (that is, singular) interface is 'roughened'. For the flat reference face the following conditions hold: $-\infty < n < 0$, $C_n = 1$, and $1 < n < +\infty$, $C_n = 0$; the reference face is placed between $n = 0$ and $n = 1$.

By using standard methods of statistical thermodynamics, Tempkin obtained the following expression for ΔG , the change of Gibbs free energy upon roughening a singular reference plane for the (001) face of a simple cubic lattice:

$$\frac{\Delta G}{Nk_B T} = \beta \left[\sum_{n=-\infty}^0 (1 - C_n) - \sum_{n=1}^{\infty} C_n \right] + \alpha \sum_{n=-\infty}^{\infty} C_n (1 - C_n) + \sum_{n=-\infty}^{\infty} (C_n - C_{n+1}) \ln (C_n - C_{n+1}), \quad (1)$$

where

$$\alpha = 4\varepsilon/k_B T, \quad \beta = \Delta\mu/k_B T. \quad (2)$$

2ε is the energy gain upon formation of two solid-liquid bonds by replacing a solid-solid bond and a liquid-liquid bond. $\Delta\mu$ is the change in chemical potential where a solid-like molecule is converted into a liquid-like molecule, i.e. $\Delta\mu$ is the difference in chemical potential if the two phases are not in thermodynamic equilibrium. k_B is the Boltzmann constant and T the temperature. A self-consistent equation can be obtained from (1) by minimizing ΔG with respect to C_n . This leads to the following equation:

$$[(C_n - C_{n+1})/(C_{n-1} - C_n)] \exp(-2\alpha C_n) = \exp(-\alpha + \beta), \quad (3)$$

which has to be solved numerically. Main results of Tempkin model are summarized below:

(i) The interface is sharp for high values of α and is rough and broad for low α . There is no 'roughening' transition as α is lowered, but the interface can be considered rough for $\alpha \lesssim 1$ and sharp (or flat or singular) for $\alpha \gtrsim 4$. For most metals $\alpha \simeq 1$ and so the interface is rough.

(ii) For nonequilibrium interfaces with $\beta \neq 0$, the Tempkin model predicts two regions in the β - α plane separated by a continuous line originating at $\beta = 0$, $\alpha \simeq 1.1$. In the region with higher α and lower β , there is a stable interface, whereas in the other region there is no stable solution to (3). In the latter region, Tempkin's model predicts continuous growth for infinitesimal β . For example, for most metals, Tempkin's model predicts continuous growth even for $\beta \simeq 10^{-5}$. For organic crystals like salol with

interface it is not possible to discriminate between a solid-like and a liquid-like molecule. Another drawback is its failure to describe the semi-crystalline topological order present at the interface; C_n is just an average density. A more detailed description is desirable.

Such a description has been provided recently (Haymet and Oxtoby 1981; Oxtoby and Haymet 1983) in a molecular theory of the crystal-melt interface by generalizing the order parameter description of freezing developed by Ramakrishnan and Yussouff (1979). The central point of the Haymet-Oxtoby formalism is that the interface is treated as a perturbation about the homogeneous liquid phase. The main assumption of this work is that the interface is sufficiently broad, compared to the molecular diameter, so that a square-gradient approximation on the spatial variation of the order parameters can be made. The order parameters describe the inhomogeneous density distribution at the interface which is assumed to be of the following form

$$\rho_l(\mathbf{r}) = \rho_l[1 + \phi_0(\mathbf{r})] + \rho_l \sum_n \phi_n(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r}), \quad (4)$$

where ρ_l is the average equilibrium density of the liquid phase and the $\mathbf{G}$ are the reciprocal lattice vectors (RLV) of the crystalline solid phase. ϕ_0 and ϕ_n are the order parameters that characterize the structure at the liquid-solid interface. They are analogues of the C_n of Tempkin's model. These order parameters are zero in the pure liquid phase far from the interface and have constant non-zero values in the pure solid phase. It is assumed that these order parameters change smoothly from their liquid-like to solid-like values as the interface is traversed from liquid to solid.

Oxtoby and Haymet (1983) obtained a set of self-consistent differential equations for the variation of ϕ_0 and ϕ_n and solved these equations numerically for planar *bcc* 100 and 111 crystal-melt interfaces. Their calculations show that the interfacial transition zone is quite broad, which is consistent with their starting assumption. One interesting prediction of the theoretical calculations is the existence of a 'structured liquid' region in the interface characterized by a liquid-like average density, but solid-like topological ordering.

It is obvious from the preceding discussion that the diffuse interface model of Haymet and Oxtoby (proposed originally by Cahn 1960) predicts a picture of the solid-liquid interface that is considerably different from that of Tempkin. In Tempkin's model, the *microscopic* boundary between solid and liquid is sharp, even after the 'roughening' of the surface. Recent investigations of Weeks and coworkers (Weeks and Gilmer 1979) have clearly shown the presence of a roughening transition for a solid-vapour interface. For a Lennard-Jones system, the roughening temperature, T_R , is below the triple point. So, this roughening transition may be of little relevance to a solid-liquid interface since the density of the liquid even at a temperature slightly above the triple point is at least an order of magnitude larger than that of the vapour. Thus, a description of the solid-liquid interface cannot be based on models which are primarily designed to describe a solid-vapour interface. A dense liquid is characterized by considerable amount of short range order. Any theory of the solid-liquid interface must pay attention to this local structure in dense liquids. This view may be further

in the vapour phase. Thus, for many properties, one can distinguish between a molecule in the solid and in the vapour state. Such a clear demarcation does not exist at a microscopic level for the solid-liquid interface; there is not sufficient separation in time scales of motion of a molecule in two adjacent layers. Thus, a diffuse interface model, in which a gradual change in atomic arrangements occurs over several molecular layers, seems more appropriate. This view finds support in results of recent computer simulations of solid-liquid interfaces.

In this paper we assumed a diffuse interface model to describe the dynamics of crystal growth from a supercooled melt. Our theory pays proper attention to the local structure of the liquid. A considerable amount of work need to be done before a detailed comparison of this theory with experiment can be made. We now briefly discuss the theory.

3. A molecular theory

We shall consider the growth of a perfect crystal from its supercooled melt. Because of supercooling, there will be a thermodynamic driving force towards solidification at the interface which will favour advancement of the crystalline front. In addition to supercooling, the velocity of crystal growth will be determined by two other factors: the rate of removal of the latent heat generated by solidification and the viscous forces present in the liquid which inhibit the formation of crystalline order. Thus the process of crystal growth is complicated due to the involvement of several dynamical processes of varying temporal and spatial dependences.

For a crystal to grow into the adjacent melt, several microscopic processes must occur simultaneously. Firstly, a transport of mass is involved because the crystal is denser than the liquid. For many solid-liquid transformations, the fractional density change involved is substantial, often 10–20% of the density of the liquid. Even for a much smaller fractional density change (as is the case for liquid metals), it may play an important role in crystal growth because it is a locally conserved variable and in a high density liquid, especially at the solid-liquid interface, transport of particles is a slow process. Secondly, the periodic arrangement of particles must build up from the spatially random liquid structure. An important point here is that the interface is rather narrow. Thus, the local structure of the liquid is important in the crystallization process. One can approximately distinguish between two regions within the interface. In the region close to the solid surface, the density and atomic arrangements will be solid-like, whereas in the region close to the liquid side, the opposite is true. For a slow steady growth of the crystal, these quantities (the density and the topological order) are expected to evolve slowly towards their solid phase values. In this limit, one can generalise the order parameters ϕ_0 and ϕ_n of (4) to the time domain and expand the time dependent singlet distribution function in the following form:

$$n(\mathbf{r}, t) = \rho_l [1 + \phi_0(\mathbf{r}, t)] + \rho_l \sum_n \phi_n(\mathbf{r}, t) \exp(i \mathbf{G} \cdot \mathbf{r}). \quad (5)$$

As before, ϕ_0 represents the time dependence of the fractional change in density, averaged over a unit cell of the lattice, and ϕ_n represents the time dependence of the oscillatory part in density. Such a separation is meaningful because the magnitudes of $\mathbf{G}$'s are large.

It is worth pointing out that ϕ_0 and ϕ_n are coupled. So, crystal growth is a process where a locally conserved variable (ϕ_0) (in a coarse-grained description) is coupled to a nonconserved variable (ϕ_n). In the terminology of time dependent statistical mechanics, such a process corresponds to the model C of the time dependent Ginzburg-Landau (TDGL) theories discussed by Hohenberg and Halperin (1977). One objective of this work is to obtain equations of motions for ϕ_0 and ϕ_n from a model kinetic equation for $n(r, t)$.

The kinetic equation proposed by Bagchi and Kirkpatrick (1986) is a non-linear diffusion equation that contains a mean-field force term due to the liquid structure present on small length scales and a term due to the temperature variation at the interface. The equation is given by

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = \nabla \cdot \bar{\mathbf{D}}(\mathbf{r}, t) \cdot [\nabla n(\mathbf{r}, t) - \beta n \mathbf{F}] - \nabla \cdot \bar{\mathbf{D}} \cdot n \nabla \ln \beta, \quad (6)$$

where $\bar{\mathbf{D}}(\mathbf{r}, t)$ is the position and time dependent self-diffusion tensor, $\beta = [k_B T(\mathbf{r}, t)]^{-1}$ and $F(\mathbf{r}, t)$ is the mean-field force term given by

$$\beta F(\mathbf{r}, t) = \nabla \int d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}', t), \quad (7)$$

$c(r)$ is the two particle direct correlation function.

The justification for using a non-linear diffusion equation to describe the dynamics of crystal growth has been discussed elsewhere (Bagchi and Kirkpatrick 1986). Here we briefly mention the salient points. Firstly, (6) has correct limiting properties. At equilibrium, the solution of (6) is the standard mean-field expression for the inhomogeneous density distribution that has been used successfully in the theory of freezing. In a homogeneous system in the absence of a temperature gradient, (6) leads to an expression for the dynamic structure factor $S(k, \omega)$, which can describe neutron scattering by dense classical liquids fairly well for large values of the wave vector $\mathbf{k}$. Secondly, recent work of de Schepper and Cohen (1982), and also of Kirkpatrick (1985), on short wavelength collective modes show that the dynamics at large wave numbers are dominated by a self-diffusion-like mode alone. Thirdly, the mean free path in a liquid at freezing density is extremely small, only 3–5% of molecular diameter. This last fact implies that in a dense liquid a hydrodynamic-like description can be used to describe processes taking place on a molecular scale.

Next, we substitute (5) for $n(\mathbf{r}, t)$ in (7) to obtain an expression for $F(\mathbf{r}, t)$. Equations (5) and (6) are then combined to obtain an equation of motion for the order parameters. The resulting expression is rather complicated. We write it in the following form

$$\begin{aligned} \frac{\partial \phi_0}{\partial t} + \frac{\partial}{\partial t} \sum_n \phi_n(\mathbf{r}, t) \exp(i \mathbf{G}_n \cdot \mathbf{r}) &= [A(\mathbf{r}, t) - \rho_l \sum_n Q_{n, -n}(\mathbf{r}, t)] \\ &+ \rho_l \sum_n B_n(\mathbf{r}, t) \exp(i \mathbf{G}_n \cdot \mathbf{r}) - \rho_l \sum_{\substack{n, m \\ \mathbf{G}_n \neq -\mathbf{G}_m}} Q_{n, m}(\mathbf{r}, t) \exp[i(\mathbf{G}_n + \mathbf{G}_m) \cdot \mathbf{r}], \quad (8) \end{aligned}$$

where the coefficients A , B_n and $Q_{n, m}$ are functions of the order parameters ϕ_0 and ϕ_G , of D and T , and of their spatial derivatives. Expressions for A , B and Q are given

equations is similar to the ones obtained from the time dependent Ginzburg-Landau description, with one important difference. In our formalism, we have explicit expressions for the coefficients that occur in the expansion of the free energy functional in the order parameters. Another aspect of (8) is that it is derived from a kinetic equation (6) and so is expected to be valid in nonequilibrium situations.

Equation (8) must be supplemented with an equation of motion of the temperature field $T(r, t)$. In principle, one should be able to express the rate of change of $T(r, t)$ in terms of the rate of change of the order parameters, and the thermal diffusion coefficient. Collins and Levine (1985) have recently initiated such an approach to the problem of diffusion limited crystal growth. The basic idea here is that as the crystalline front advances into the liquid, the order parameters change from liquid-like to solid-like values giving rise to latent heat of fusion which must be removed from the interface by thermal diffusion. So, we should find an expression for the *local* latent heat of fusion (that is, a position dependent entropy change) in terms of the order parameters. We shall leave this task for the future. In this paper we shall assume a linear temperature gradient across the interface and find an expression for the velocity of steady growth of a planar crystal surface.

Let us assume that the crystal is growing in the z -direction with a constant velocity V . In the coordinate frame attached to the moving surface, ϕ_0 , ϕ_n , D and T will be approximately independent of time for a slowly advancing interface and their dependence on the position coordinate z will be similar to that of a stationary equilibrium interface. The first term on the right hand side of (6) will then be small and negligible. Making the coordinate transformation

$$z_1 = z + Vt, \quad (9)$$

we obtain

$$\frac{\partial}{\partial t} n(z_1 - Vt) = \frac{\partial}{\partial z_1} D(z_1 - Vt) n(z_1 - Vt) \times \frac{1}{T} \frac{\partial}{\partial z_1} T(z_1 - Vt). \quad (10)$$

The time derivatives of the order parameters are given by

$$\begin{aligned} \frac{\partial}{\partial t} \phi_0(z_1 - Vt) &= -V \frac{\partial \phi_0}{\partial z_1}, \\ \frac{\partial}{\partial t} \phi_n(z_1 - Vt) &= -V \frac{\partial \phi_n}{\partial z_1}. \end{aligned} \quad (11)$$

Using (11) and (5) in (10) and keeping only the terms that are multiplied by $(\mathbf{G}_n \cdot \hat{\mathbf{z}})$ because they are the dominating terms, we obtain the following simple expression for V

$$V = -\frac{1}{z_w} \int_{z_s}^{z_l} dz D(z) \frac{1}{T} \frac{\partial}{\partial z} T(z), \quad (12)$$

where z_w is the width of the interface, and z_l and z_s denote positions where the order parameters reach their liquid-like and solid-like values, respectively. If we further assume a linear dependence of $T(z)$ on z , we recover the usual linear dependence (Cahn 1960) of V on ΔT —the temperature difference between the crystal and the melt.

4. Discussion

An analysis (Langer 1980) of the thermal diffusion equation with the usual equilibrium Joule-Thomson boundary condition shows that a steady-state solution for the thermal field is possible only for a unique supercooling ($T(-\infty) = T_m - L/C_p$ where T_m is the equilibrium melting temperature, L the latent heat and C_p the specific heat). At this supercooling, the crystal growth velocity is arbitrary (Langer 1980). As discussed by Collins and Levine (1985), this is simply because of the absence of any length scale in the problem. In the analysis of Bagchi and Kirkpatrick (1986), the length scale is determined by the variation of the order parameters in the interface and this gives rise to a well-defined velocity of growth of a planar interface, as given by (12).

It is interesting to compare our theory with Cahn's original (Cahn 1960) theory of crystal growth. The fundamental ideas are quite similar. The main difference is that our work is more microscopic and pays proper attention to the structure at the solid-liquid interface. This has been possible because of our use of the nonlinear diffusion equation (6) to describe the dynamics at the interface.

A limitation of this work is that it is based on a mean-field description of the potential experienced by the particles at the interface. However, the justification of using a mean-field description in the present problem comes from the following observations. Firstly, such a description has been successfully used in the theories of freezing. Secondly, it gives fairly accurate description of the dynamic structure factor, $S(k, w)$, for large values of k . Since dynamics of freezing involves variations on molecular length scales, a description at the level of the mean-field may be fairly accurate.

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Why are certain substances metallic?

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Abstract. Metallic properties are by no means confined to elemental substances alone. A variety of materials, both inorganic and organic, show metallic properties. Some of these exotic substances exhibit electrical conductivities comparable to those of elemental metals like copper. A large number of systems traverse the transition from the metallic state to the non-metallic state when there is a change in temperature, pressure or composition. Metal oxides provide a wide range of materials exhibiting metallic behaviour or going through the metal to non-metal (*M-NM*) transition. Alkali metal-ammonia solutions, with which chemists are all too familiar, probably constitute one of the earliest and most widely studied examples of the *M-NM* transition. However, a proper recognition of the metallization of ammonia in the context of the variety of solid systems exhibiting *M-NM* transitions has only been possible recently. Another interesting class of substances is that of expanded metals such as Hg and Cs which become non-metallic when the density is reduced below a critical value. Several organic solids, metal-chain compounds and polymers are not only metallic, but also become superconducting at low temperatures. With such a galaxy of chemical substances exhibiting metallic behaviour, the fundamental, recurring question of vital interest is “what makes a metal?”. In this contribution, we shall examine operational criteria as well as criteria derived from models to answer this question. A related question of equal interest to chemists is “how many atoms are necessary to bring about metallic properties?”.

Keywords. Metal–non-metal transitions; metal-ammonia solutions; expanded metals; low-dimensional conductors; metallicity criteria.

1. Introduction

Metals have played a key role in man's life from time immemorial. A large majority of the elements on this planet are metallic under ambient conditions. Traditionally, lustre, high density and other characteristic physical properties have been associated with the metallic state and they are generally valid for solid elements such as copper and gold. Such notions met with unexpected difficulties when Davy discovered sodium and potassium in 1807, which possessed some of the properties attributed to metals but had extremely low densities. We also have metals such as mercury and cesium which are ordinarily liquids. More significantly, metallic behaviour is not confined to elements alone (Edwards and Rao 1985). Many metal oxides (e.g. LaNiO_3 , ReO_3 , CrO_2 , TiO) and sulphides (e.g. TaS_2 , NbS_3 , $(\text{SN})_x$, $\text{Sm}_{0.85}\text{Gd}_{0.15}\text{S}$) exhibit metallic properties; some of them become superconducting at low temperatures. Metallic behaviour extends to organic solids as well and several organic ‘metals’ have been discovered in the last few years. There is also the fascinating class of solids which are non-metallic under

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certain conditions but become metallic with change in temperature, pressure or composition (Mott 1974; Edwards and Sienko 1983; Edwards and Rao 1985). Typical examples of materials which exhibit such transitions with change in temperature or pressure are Ti_2O_3 , VO_2 , V_2O_3 , La_2NiO_4 , LaCoO_3 , NiS and SmS . Related series of compounds of the same transition metal exhibit a wide range of electrical and related properties as exemplified by the oxides of Ti, V and Cr (Rao and Subba Rao 1970; Goodenough 1971). TiO_2 is an insulator while TiO is a metal; Ti_2O_3 and some members of the $\text{Ti}_n\text{O}_{2n-1}$ family undergo metal to non-metal (*M-NM*) transitions. V_2O_5 is an insulator while VO is a semi-metal; Cr_2O_3 is an insulator but CrO_2 is a metal. Examples of solids traversing the *M-NM* transition with change in composition include phosphorus-doped silicon and metal oxides such as $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ and Na_xWO_3 . Similar composition-controlled metal-non-metal transitions are exhibited by metal solutions in non-aqueous solvents (e.g. ammonia, methylamine). Then there are metals such as mercury and cesium which become insulating on expansion through a critical temperature and density.

Theoretical investigations to distinguish the metallic and the non-metallic states of solids have been made ever since the beginning of quantum mechanics and criteria for metallic character have been derived based on these studies. Attempts have also been made to relate atomic properties of elements in the free state with metallic or non-metallic properties in the condensed state. In this article, we shall briefly present an overview of systems exhibiting metallic behaviour as well as those traversing the metal to non-metal transition in the condensed state and discuss the important criteria for metallic character. We shall also examine the various models for metal-non-metal transitions in solids and the question as to how many atoms make a metal.

2. Operational criteria for metallicity

Several operational criteria can be employed to distinguish metals from non-metals. For example, photo-electron spectra of metals clearly show a sharp rise in the density of states at the Fermi energy unlike non-metals. In figure 1 we show typical valence band spectra of some oxides to demonstrate how the spectra of metals are characteristically different from those of insulators. We cannot, however, employ the density of states and

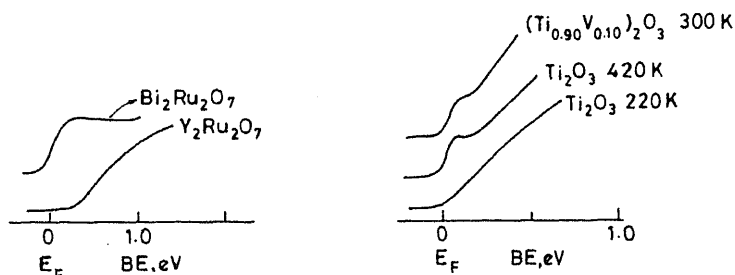


Figure 1. HeI photoelectron spectra of oxides in the valence band region showing the difference between metals and non-metals (Egdell and Goodenough 1983; Rao and Sarma 1982). $\text{Bi}_2\text{Ru}_2\text{O}_7$ is a metal while $\text{Y}_2\text{Ru}_2\text{O}_7$ is a non-metal. Ti_2O_3 becomes metallic above 410 K; $(\text{Ti}_{0.90}\text{V}_{0.10})_2\text{O}_3$ is metallic.

other properties related to the Fermi surface as criteria for metallic character since many metals are liquids. Magnetic properties can also be used to distinguish the metallic and the non-metallic states. For example, Pauli-paramagnetic behaviour is found in metals because of the presence of itinerant electrons while Curie behaviour is found in non-metals since they possess localized electrons. Similarly, optical properties; especially reflectance (lustre), can be used as a criterion. In fact, lustre has been the traditional characteristic attributed to metals such as gold. Reflectance spectra of metals show a sharp cut-off at the plasma frequency.

While the different considerations mentioned above provide a qualitative basis for describing metals, the best criterion appears to be electrical resistivity. The electrical resistivity of a metallic substance tends to a finite value (or zero in a superconductor) as the temperature tends to absolute zero, while in an insulator the resistivity tends to infinity. Accordingly, the electrical resistivity of a material very close to absolute zero provides a definitive operational criterion to distinguish metals from insulators. In figure 2 we show the electrical resistivity behaviour of a few oxides of transition metals to illustrate how 'metallic' some of them are compared to an elemental metal like copper. The resistivity behaviour of silicon samples doped with different concentrations of phosphorus is shown in figure 3. The figure shows how the metal to non-metal

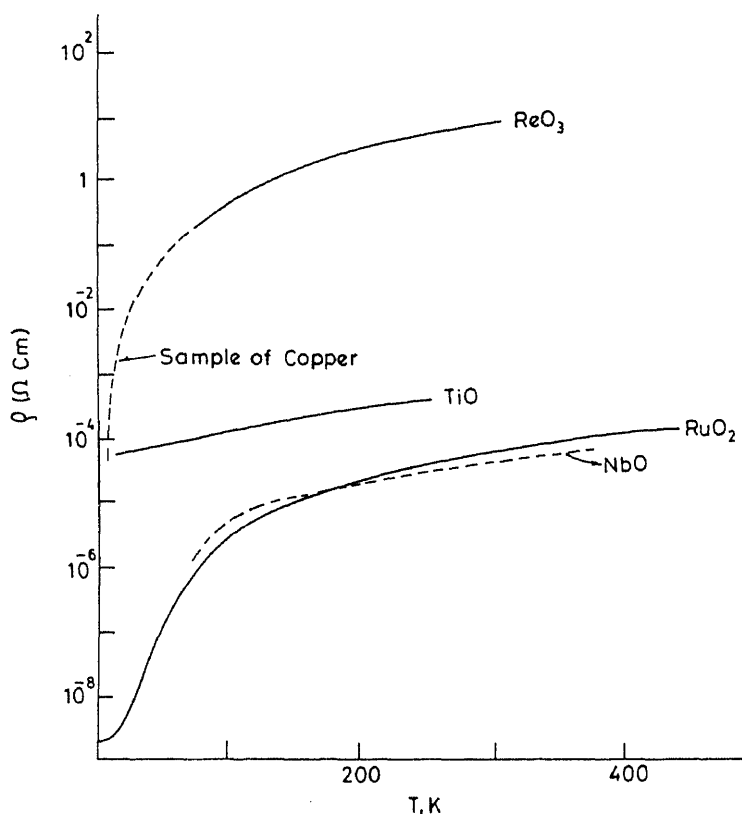


Figure 2. Electrical resistivity behaviour of a few oxide metals.

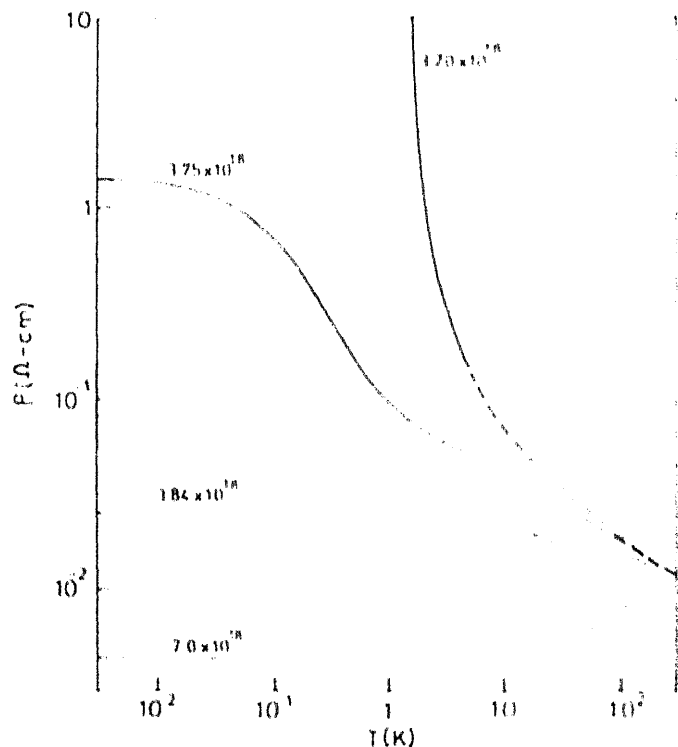


Figure 3. Electrical resistivity behaviour of phosphorus doped silicon (Rosenbaum 1980, 1983). Concentrations of phosphorus are shown.

transition occurs at a concentration of around 3.7×10^{18} electrons cm^{-3} . In figure 4 show how the temperature dependence of the electrical conductivity varies with the concentration of Au in the $\text{Cs}_{1-x}\text{Au}_x$ system (Hensel 1980). Around $x = 0.5$ the temperature dependence of conductivity changes from negative to positive. In the insulating state, the alloy is best described as Cs^+Au^- . The change in sign of the temperature coefficient of resistivity undoubtedly provides a clear indication of the M - NM transition in materials.

Based on these various operational criteria, chemists have distinguished metals from non-metals and have systematized elements in the periodic table. 79 out of the

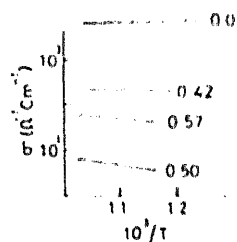


Figure 4. Electrical conductivity of the $\text{Cs}_{1-x}\text{Au}_x$ system (Hensel 1980).

s-block										p-block																
H		He																								
IA		IIA		d-block														III A					IV A	VA	VIA	VIIA
Li		Be																B	C	N	O	F	Ne			
Na		Mg		III B	IV B	VB	VIB	VIIB	VIII			IB	IIB	Al	Si	P	S	Cl	Ar							
K		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr								
Rb		Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
Cs		Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn								
Fr		Ra																								

Table 1. Some examples of metallic and non-metallic states of matter.

	Non-metallic	Metallic
Elements	Si (s) H ₂ (g)	Si (l) at $T > 2270$ K H ₂ (s) under high pressure
Alloys	Cs _{1-x} Au _x (l)	Cs _{1-x} Au _x (l)
Doped semiconductors	P: Si (s) below critical concentration of P	P: Si (s) above critical concentration of P.
Metal-rare gas films	Na: Ar (s) Pb: Xe (s) below critical concentration of metal	Na: Ar (s) Pb: Xe (s) above critical concentration of metal
Metal oxides (all solids)	MgO V ₂ O ₃ at $T < 160$ K Na _x WO ₃ ($x < x_c$) La _x Sr _x CoO ₃ ($x < x_c$)	ReO ₃ , TiO V ₂ O ₃ at $T > 160$ K Na _x WO ₃ , ($x > x_c$) La _x Sr _x CoO ₃ ($x > x_c$)
Organic solids	Naphthalene, anthracene, (CH) _x pure and or small dopant concentration (dopant = AsF ₅ , ClO ₄ , Na)	TTF-TCNQ, (CH _x) higher dopant concentration
Solid polymers	Polyethelene, PVC	(SN) _x organometallic polymers.
Metals in solvents	Na in liquid NH ₃ ($x < x_c$)	Na in liquid NH ₃ ($x > x_c$)
Expanded metals	Liquids: Hg, Cs, at high T ($T > T_c$) $T_c = 1750$ K (Hg); 1925 K (Cs)	Liquids: Hg, Cs ($T < T_c$)
Expanded metal compounds	Li (CH ₃ NH ₂) ₄	Li (NH ₃) ₄ , Ca (NH ₃) ₆

metallic behaviour is observed above a particular concentration of the metal. The case of expanded metals such as Hg and Cs was mentioned earlier. Having cited examples of *M-NM* transitions, the question that we have to answer is 'When does a metal transform to a non-metal?'. Accompanying this query is the inseparable question 'What makes a metal?'. In what follows we shall attempt to answer these two fundamental questions in which all chemists should be interested.

4. Theoretical models and criteria for metallization

The earliest theoretical attempt to explain differences between the metallic and the non-metallic states of solids was by Wilson who employed the free electron theory of Bloch (independent electron approximation). The Schrödinger equation for an electron moving in a periodic field of potential $U(x, y, z)$ is given by

$$\nabla^2\psi + (2m/\hbar)^2 \{E - U(x, y, z)\} \psi = 0, \quad (1)$$

where ψ is of the form $\exp(ikr)U(x, y, z)$; $U(x, y, z)$ has the period of the lattice and k is the wave vector. This approach gives a description of the electron energy levels in terms of a family of continuous functions (bands), each possessing the lattice periodicity, giving rise to two distinct configurations: an insulator where the energy bands are full and a metal where the highest occupied band is only partially filled (figure 6). The model explains the electrical properties of simple metals including oxidic metals such as ReO₃ (figure 7).

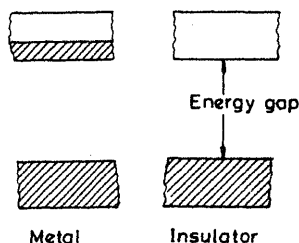


Figure 6. Band picture of a metal and an insulator.

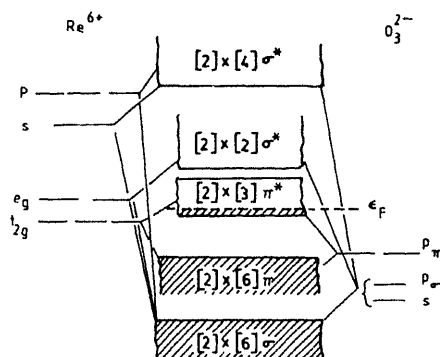


Figure 7. One-electron band diagram of ReO_3 (Goodenough 1971).

For example, oxides such as MnO and CoO possessing the rocksalt structure are all insulators even though they have partially filled d -bands. At first sight this might not appear too surprising to chemists familiar with the localized-electron descriptions of transition metal complexes. However, TiO , on the other hand, is metallic and becomes a super-conductor below 2K. Curiously, the shortest metal-metal distance in TiO (along the diagonal in the (100) plane between the metal t_{2g} orbitals) is 2.94 Å while in MnO and CoO , it is 3.01 and 3.14 Å respectively. Apparently, there is a critical metal-metal distance (or overlap) only below which these metal oxides become metallic (Goodenough 1971). The critical overlap integral or distance is larger than the metal-metal distance in insulating MnO , FeO , CoO and NiO ; in metallic TiO , the metal-metal distance is shorter than the critical distance while in VO , which is a semi-metal, they are nearly comparable.

The failure of the Bloch-Wilson scheme can be understood when we examine the case of an assembly of alkali atoms at different densities. At high densities, when the metal-metal separation is small, there is considerable overlap of the $6s$ wave functions giving rise to the half-filled band responsible for the metallic behaviour. At small densities (large metal-metal distances), the Bloch-Wilson scheme would still predict metallic

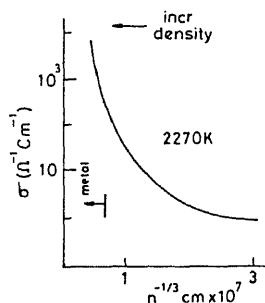


Figure 8. Electrical conductivity of cesium as a function of the cube root of the electron density (Hensel 1971). Metal-non-metal transition is indicated.

repulsion is reduced (screened) via the degenerate sea of electrons. Hubbard (1964) proposed a model which comes to grips with the problem of itinerant (band) and localized behaviour of electrons at high and low densities respectively.

According to the Hubbard model, the Coulomb repulsion energy, U , between two electrons on the same atom becomes more significant at low densities of the alkali metal (as in the atomic case) while the band width, Δ , becomes the determining factor at high densities (figure 9). In the atomic limit, U is the difference between the ionization energy and the electron affinity. The ratio (Δ/U) then provides a basis for distinguishing metals from non-metals (or insulators). According to this model, the condition for metallization is

$$(\Delta/U)_{\text{critical}} \gtrsim 1.2. \quad (2)$$

Based on dielectric screening properties of a uniform electron gas, Mott (1949) proposed a model to distinguish metals from non-metals. This model is independent of the atomic arrangement in the solid. The valence electrons are trapped in the coulomb field in the atomic state while in a metal the attractive interaction is screened (reduced) via the itinerant electrons. The screening potential is of the form,

$$V(r) = (-e^2/r) \exp(-qr), \quad (3)$$

where r is electron-cation separation. The characteristic screening length q^{-1} (which

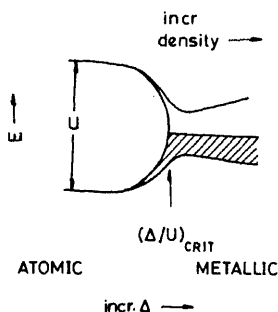


Figure 9. Metal-non-metal transition occurs at a critical value of (Δ/U) according to the Hubbard model (Hubbard 1964)

depends on the electron density, n is rather small in metals. According to the model, there will be a first-order metal to non-metal transition (the Mott transition) when $V(r)$ has localized, bound states. The condition for such states to occur is given by

$$n_c^{1/3} a_H^* \approx 0.25, \quad (4)$$

where n_c is the critical concentration for metallization and a_H is the effective Bohr-orbit radius. Based on an analysis of extensive experimental data (see figure 10), Edwards and

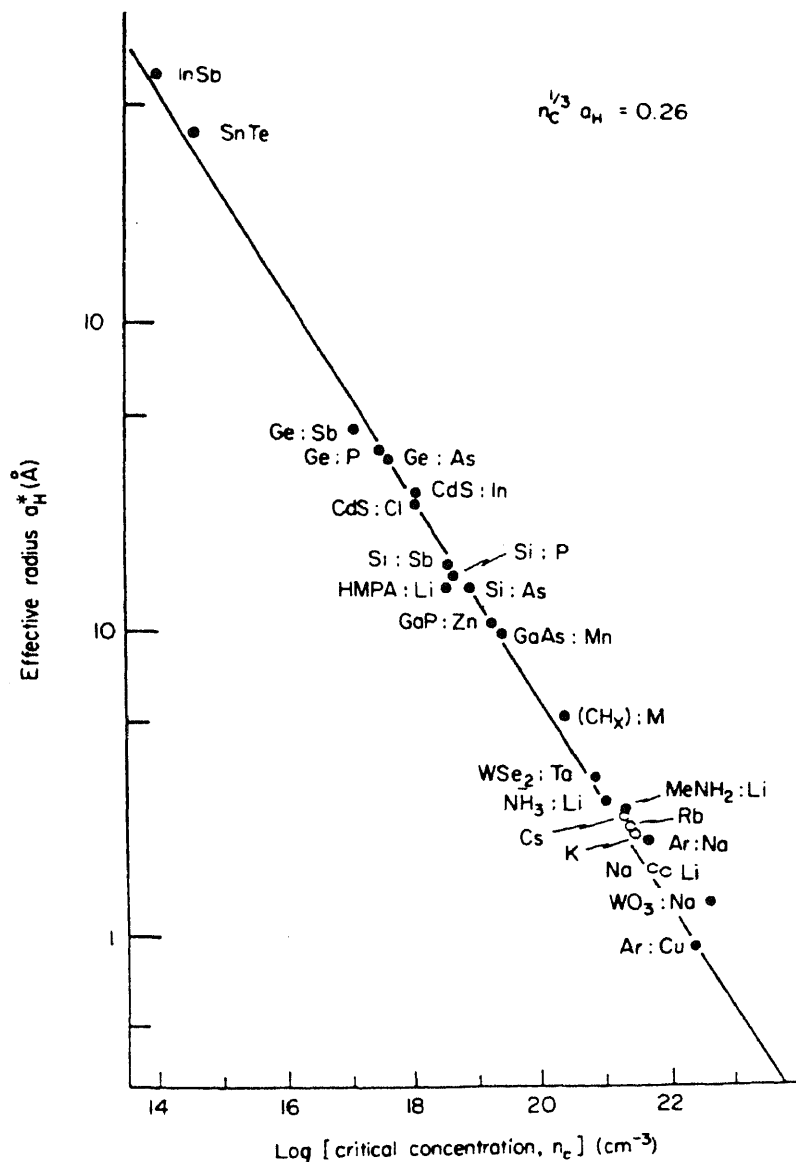


Figure 10. Logarithmic plot of the Bohr radius against the critical electron concentration for metallization (Edwards and Sienko 1981).

Sienko (1981) have found that

$$n_c^{1/3} a_H^* \approx 0.26. \quad (5)$$

One can consider the metal to non-metal transition to be essentially due to a competition between the kinetic and the potential energies of electrons. While the kinetic energy delocalizes electrons, potential energy localizes them (Ramakrishnan 1985). The condition for the kinetic energy to be greater than the potential energy is given by

$$(h^2/m^*)n^{2/3} \gtrsim A(e^2/\epsilon a_H^*)$$

or

$$n^{1/3} a_H^* = A. \quad (6)$$

The best estimate of A turns out to be 0.25 or 0.26. The potential energy in the Hubbard model is the correlation energy U .

The Herzfeld criterion: Herzfeld (1927) proposed that local field corrections in an insulator drive it to become metallic when the insulator becomes sufficiently dense. The dielectric constant, ϵ , of such a system is expressed as

$$\epsilon = 1 + (4\pi N\alpha)/[1 - (4\pi N\alpha/3)], \quad (7)$$

where α is the polarizability of atoms. When $(4\pi N\alpha/3) = 1$, ϵ diverges. The above

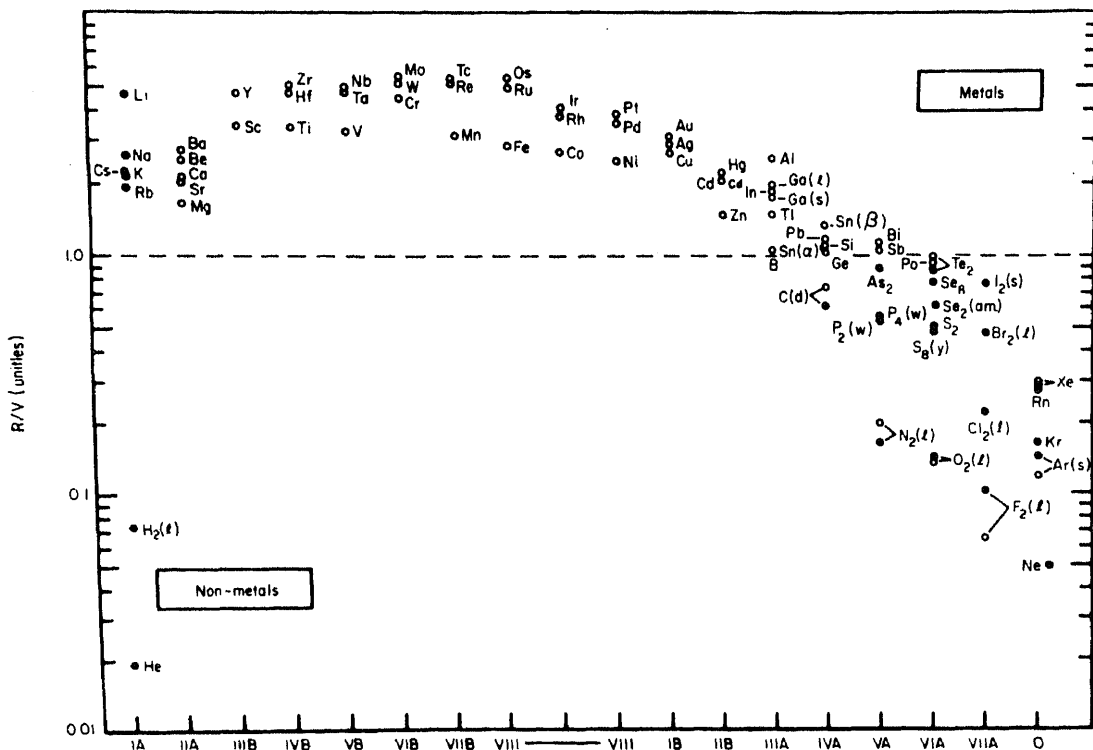


Figure 11. Metallization of elements in the periodic table as explained by the Herzfeld

equation in its simple form may not survive in dense systems (due to other processes contributing to α as atoms begin to overlap). According to Herzfeld, the characteristic frequency ν_0 of the bound electrons in atoms is diminished at finite densities to

$$\nu = \nu_0 [1 - (R/V)]^{1/2}, \quad (8)$$

where R is the molar refractivity of the atom (equal to $4\pi N\alpha/3$) in the gaseous state and V is the molar volume in the condensed state. We readily see that the metal to non-metal transition should occur depending on whether (R/V) is less than or greater than unity.

For a metal,

$$(R/V) \geq 1,$$

for an insulator,

$$(R/V) < 1. \quad (9)$$

There has been considerable interest in detecting the polarization catastrophe at the M - NM transition. What is more pertinent to the discussion here is that the (R/V) criterion is able to explain why most elements in the periodic table under ambient

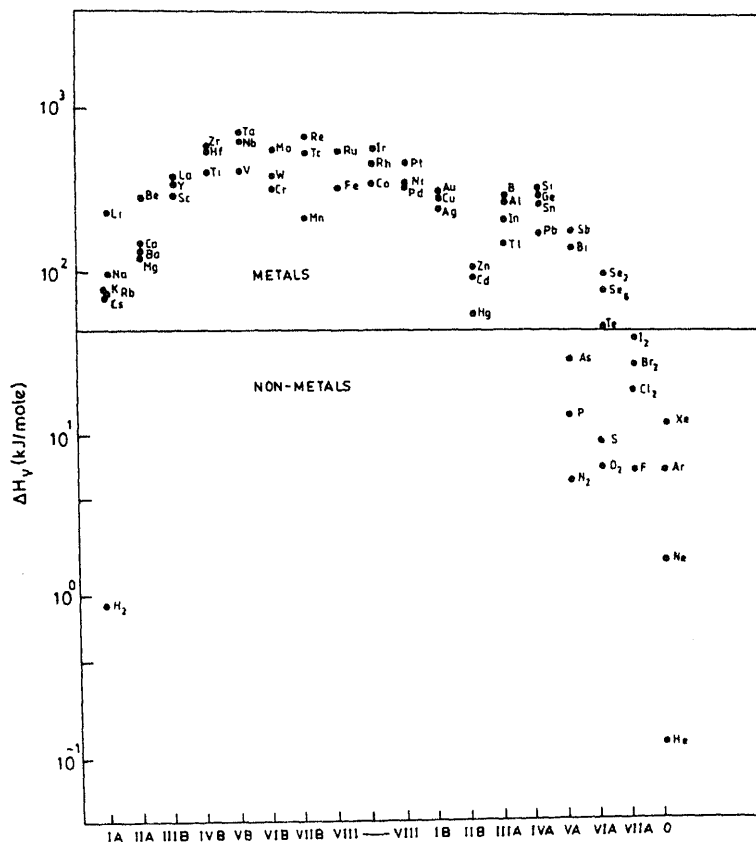


Figure 12. Latent heat of vapourization as a criterion for the metallic behaviour of elements (Rao and Ganguly 1986).

conditions are metallic in the solid state (figure 11). The criterion predicts why hydrogen is metallic at high pressures; according to this criterion, mercury is metallic because of its high density in the liquid state.

A thermodynamic criterion: A thermodynamic criterion for metallization of elements has been proposed recently based on the latent heats of vapourization, ΔH_v . Since more elements are metallic in the molten state and some metals are indeed liquid under ambient conditions, the liquid state of metals is probably more universal (at least 84 elements out of 103 being metallic in the liquid state). It is found that ΔH_v of metallic elements is greater than a critical value of 42 kJ mol^{-1} which demarcates metals from non-metals (Rao and Ganguly 1986) (figure 12). ΔH_v is not only a simple operational criterion, but is perhaps superior in some respects to the Herzfeld criterion. Furthermore, it can be shown ΔH_v itself is proportional to $(R/V)^n$, thereby indicating the link between the two criteria. This also shows the important role of the atomic polarizability in determining the metallicity of elements.

5. Different types of metal–non-metal transitions in solids

Several kinds of metal–non-metal (*M-NM*) transitions occur in solids (Mott 1974; Rao and Rao 1978; Ramakrishnan 1985). We shall discuss them with illustrative examples.

(a) *Mott transition:* This transition, discussed in an earlier section, requires a first-order transition (at 0 K) between the localized and the itinerant electron regimes (Mott 1974, 1949). Although the Mott criterion, $n_e^{1/3} a_H^* \approx 0.25$, describes the onset of metallic character in a large variety of solids over a wide range of critical electron concentrations ($\approx 10^{10}$) and of the Bohr radii (600 Å), the transition has not been found, in any simple solid, to be a function of temperature or pressure.

(b) *Transitions occurring between extended states:* These transitions can be described within the broad framework of the band theory of solids. The band structure of a solid made up of atoms with an even number of electrons can be made to change over to a situation where the empty and filled bands cross or overlap each other due to a change in pressure, temperature or suitable doping (Mott 1974; Rao and Rao 1978; Honig 1975). Such band-overlap or band-crossing transitions occur in solids such as Ti_2O_3 , VO_2 and V_2O_3 (figure 13) and they are generally accompanied by changes in crystal structure and, in some instances, in magnetic properties.

Ti_2O_3 (corundum structure) undergoes a second-order *M-NM* transition with a 100-fold jump in electrical conductivity (figure 13) accompanied by a change in *c/a* ratio around 410 K. The structure remains the same throughout and the oxide is paramagnetic across the transition. Replacement of Ti by V up to 10% makes the oxide metallic and the *c/a* ratio of the solid solution at the composition corresponds to that of the high temperature metallic phase. The *M-NM* transition in Ti_2O_3 , associated with only a small change in conductivity, arises from band crossing.

VO_2 undergoes a first-order transition (monoclinic-rutile) accompanied by a ten thousand-fold jump in conductivity at 340 K (figure 13). The material remains paramagnetic throughout. This transition can be understood in terms of a crystal distortion model where the band gap opens up in the low temperature monoclinic phase.

V_2O_3 undergoes a first-order transition (monoclinic-corundum) accompanied by an unbelievable ten million-fold jump in electrical conductivity around 160 K (figure 13).

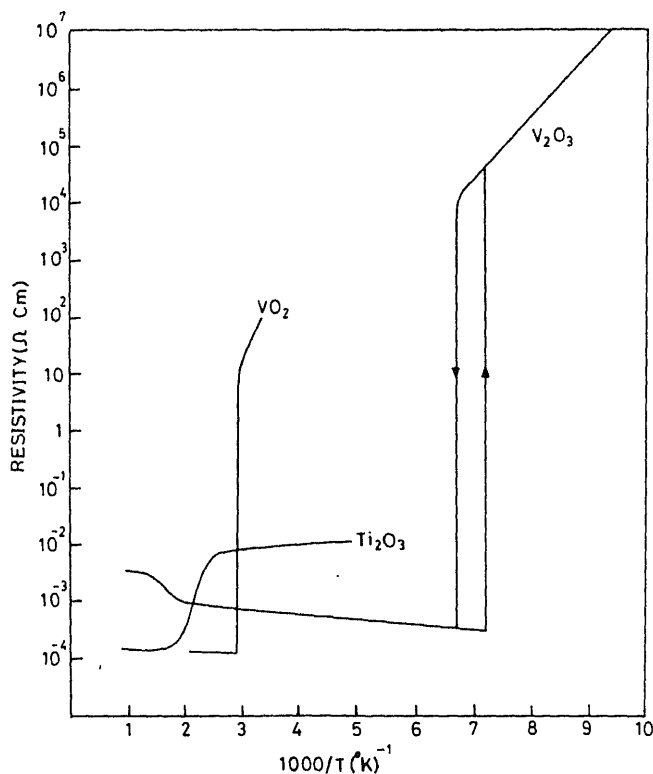


Figure 13. Metal-non-metal transition in Ti_2O_3 , VO_2 and V_2O_3 .

The transition is accompanied by a large change in c/a ratio and volume, the c/a ratio of V_2O_3 in the metallic (M) phase being the highest amongst the oxides of corundum structure. At the transition, antiferromagnetic ordering changes to paramagnetic behaviour; the 160 K transition may thus be considered to be one from the antiferromagnetic insulating (AFI) phase to the M phase. V_2O_3 also shows a second-order transition around 400 K with a small conductivity anomaly (figure 13). Application of pressure renders V_2O_3 metallic suggesting that this oxide is near the critical region. Accordingly, doping with Cr and Ti cause negative (increase in transition temperature) and positive (decrease in transition temperature) pressure effects; slight oxygen excess has the same effect as Ti doping (Honig 1982). Doping with small amounts of Cr (0.5 to 2%) changes the 400 K transition to a first-order transition from the metallic phase (M) to an insulating, paramagnetic phase (I); the temperature of the M - I transition decreases with increase in Cr concentration while that of the AFI- M transition increases. With further increase in temperature (> 400 K), the I phase transforms to a new high-resistivity metallic phase, M' . These varied features of the M -NM transitions of V_2O_3 are truly fascinating and attempts have been made to understand them on the basis of theoretical models (Rao and Rao 1978; Honig 1982).

Besides the above three oxides, several other metal oxides (e.g. Magnéli phases $\text{Ti}_n\text{O}_{2n-1}$, $\text{Nb}_n\text{O}_{2n-1}$) and sulphides (e.g. CrS and NiS) also exhibit M -NM transitions. The

LaCoO_3 and other rare earth cobalt oxides exhibit a transition around 1200 K when the e_g electrons of cobalt transform to a σ^* band (figure 14). The transformation occurs over a wide range of temperature accompanied by an increase in the Co-O overlap; above the 1200 K transition, the temperature coefficient of conductivity indicates metallic behaviour (Bhide *et al* (1972)). The value of resistivity at the transition temperature is barely $2000 \mu\Omega \text{ cm}$. It is interesting that the electrical resistivity changes of these cobalt oxides closely follow the changes in magnetic susceptibility.

It has been established recently (Rao and Ganguly 1985) that stoichiometric La_2NiO_4 possessing the K_2NiF_4 structure undergoes a M - NM transition in two dimensions only (ab plane). The transition is due to the opening of a gap in the σ^* band due to $x^2 - y^2$ correlation effects.

(c) *Valence fluctuation*: SmS shows a discontinuous transition (decrease in volume) on application of pressure (6.5 k bar) at room temperature due to the promotion of a $4f$

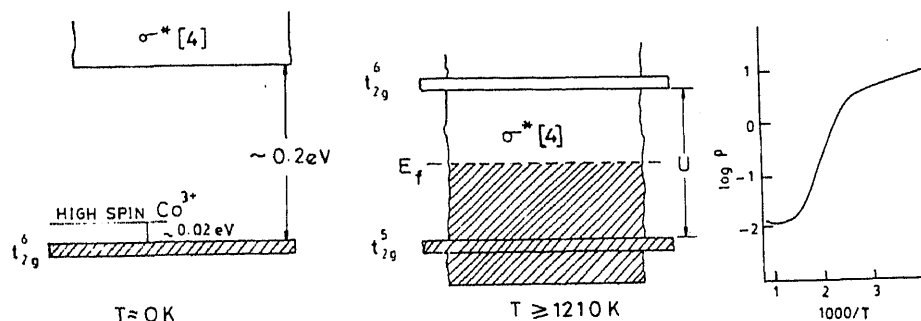


Figure 14. One-electron band picture of LaCoO_3 at 0 K and above the NM -transition (Bhide *et al* 1972). Electrical resistivity behaviour is also shown.

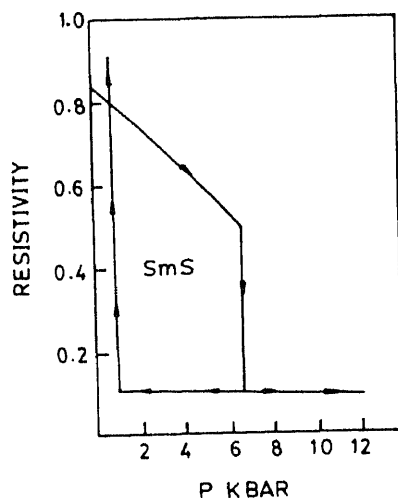
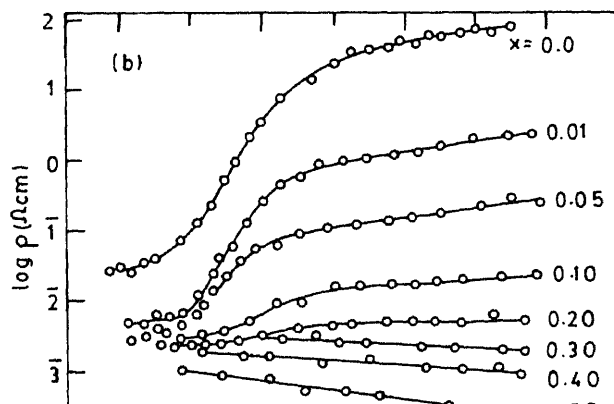
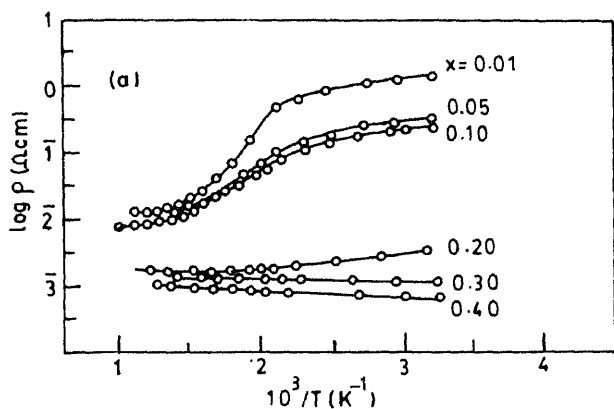


Figure 15. Electrical resistivity behaviour of SmS (Jayaraman *et al* 1970, 1973).

electron to the conduction band. The change in volume is accompanied by a sharp decrease in resistivity (figure 15), but there is no change in structure type (Jayaraman *et al* 1970). In the high-pressure metallic phase, samarium is essentially 'trivalent'. Replacement of Sm by Gd as in $\text{Sm}_{0.85}\text{Gd}_{0.15}\text{S}$ stabilizes the high pressure metallic phase at room temperature and atmospheric pressure (Jayaraman *et al* 1970). On cooling this phase, there is an explosive first-order transition (due to increase in volume) to a non-metallic phase.

(d) *Anderson transition*: Anderson (1958) proposed that introduction of sufficient disorder in a solid can effectively transform the material from a metal to an insulator. Such a disorder-induced transition from an itinerant to a localized electron state (Ramakrishnan 1985) is referred to as the Anderson transition. According to Anderson, there is a critical value of (Δ/V_0) for which electron diffusion is impossible at 0 K and a nominally metallic system becomes insulating; here, Δ is the band width and V_0 is the random potential due to disorder. Mott (1972) has proposed that there is a finite minimum electrical conductivity, $\sigma_{\min}$, in a metallic three-dimensional disordered system. At 0 K, one cannot have a non-zero value of conductivity less than $\sigma_{\min}$:

$$\sigma_{\min} = (\pi e^2 / 4z\hbar d) (\Delta / V_0)_{\text{crit}} \quad (10)$$



where d is the distance between centres at the M - NM transition. Although some of the early ideas of Mott on the mechanism of conduction in disordered solids have required some modification (Ramakrishnan 1985), the concept of minimum metallic conductivity has been found to be most useful. In fact, most experimental systems do exhibit $\sigma_{\min}$ behaviour at least above cryogenic temperatures. We shall examine the $\sigma_{\min}$ behaviour in some oxide systems where the M - NM transition is brought about by compositional changes.

LaCoO_3 and LaVO_3 are both insulators at room temperature. However, replacement of La by Sr as in $\text{La}_{1-x}\text{Sr}_x\text{BO}_3$ ($B = \text{Co}$ or V) brings about remarkable changes in properties. In both these systems when $x \gtrsim 0.3$, the material becomes metallic (Rao and Ganguly 1985). At low Sr concentrations ($x < 0.1$), the B^{4+} holes are bound to Sr^{2+} while at high x (> 0.3) the holes form a degenerate gas; in the intermediate range of concentrations disorder arising from the random distribution of Sr^{2+} and B^{4+} ions induces localization of carriers. In figure 16 we show the electrical resistivity behaviour of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ ($\text{Ln} = \text{Pr}$ or Nd). We clearly see that the M - NM transition or the change in the sign of the temperature coefficient of resistivity (TCR) occurs around $3000 \mu\Omega \text{ cm}$ which corresponds closely to Mott's value of $\sigma_{\min}$.

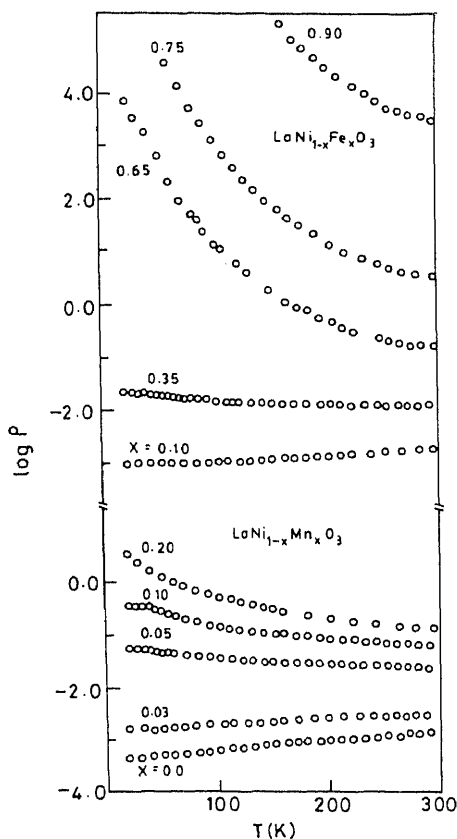


Figure 17. Electrical resistivity behaviour of $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ [$M = \text{Fe}$ or Mn] (Ganguly *et al* 1984).

Recently, electronic and magnetic properties of the $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Cr, Mn, Fe, Co}$) system have been investigated in detail (Vasanthacharya *et al* 1984; Ganguly *et al* 1984). LaNiO_3 ($x = 0$) is metallic and Pauli paramagnetic. Doping LaNiO_3 with any of the M ions makes it insulating beyond a critical value of x as shown in figure 17. Here again, the TCR changes sign around a resistivity value of $2000\text{--}3000\ \mu\Omega\text{ cm}$. In all such oxide systems including bronzes such as Na_xWO_3 , the TCR change occurs around a resistivity value ($2000\text{--}3000\ \mu\Omega\text{ cm}$) which is about ten times the value of the resistivity where the TCR of amorphous metals changes sign (Mooij 1973; Rao and Ganguly 1985). This is not entirely surprising since the electron concentration in oxides is smaller than in amorphous metals. What is significant is that $\sigma_{\min}$ serves to demarcate the metallic and non-metallic regimes so successfully (Rao and Ganguly 1985).

4. Metal clusters

Alkali metal clusters are known to occur in the vapour phase and they have considerably lower ionization energies than isolated atoms. Today, we have several ways of preparing clusters of metal atoms of varying sizes. Metals such as cesium form larger clusters with increase in density (starting from isolated atoms in dilute vapours); as the density approaches a critical value, electrical conduction is facilitated (figure 8). The interesting question that one has to answer is 'how many atoms are needed within a cluster to obtain metallic properties?'. Metallic conduction would require complete delocalization of electrons requiring a large number of atoms in the cluster, spin delocalization would, however, require a smaller number of atoms (Harrison and Edwards 1985). Metal particulates (as present on the surface of supported metal catalysts) constitute an aggregate somewhere between large metal atom clusters and the bulk metal. In figure 18 we have schematically depicted the atom, the cluster and the bulk metal regimes. While localized electron states would be present in discrete atoms and small clusters, quantum-size effects (Harrison and Edwards 1985) may well be found in large clusters.

In the last few years, a variety of compounds containing metal clusters bound to ligands (figure 19) have been synthesized (Lewis and Green 1982). In small-nuclearity cluster compounds the electrons are paired, but in high nuclearity cluster compounds electron levels are expected to be closely spaced. Magnetic susceptibility studies seem to indicate evolution of certain aspects of metallic behaviour in high nuclearity compounds (Johnson *et al* 1985). Metal cluster compounds also serve as model

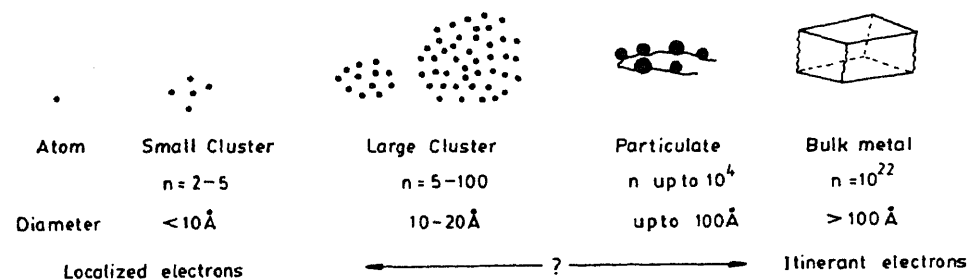


Fig. 18. Metal clusters, metal clusters and bulk metal.

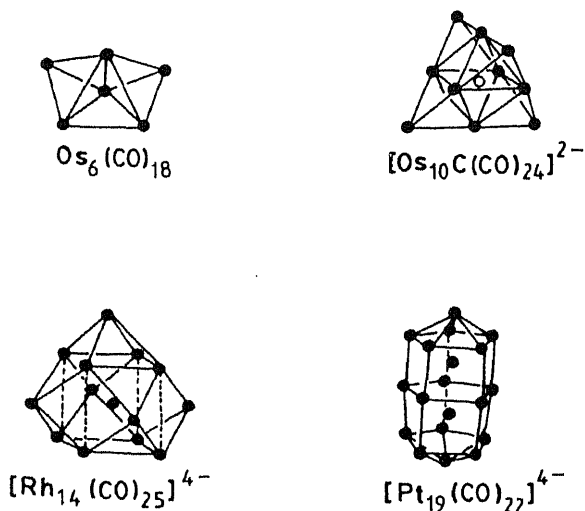


Figure 19. Typical metal cluster compounds.

compounds for surface species produced by the interaction of molecules with metal surfaces.

7. Metal-ammonia solutions

Solutions of alkali metals in liquid ammonia are blue and ionically conducting when dilute. In the bronze coloured, concentrated solutions, the electrical conductivity is in excess of that of liquid mercury. Over the intermediate composition range (1 to 7 mol % metal*) a *M-NM* transition takes place with quite striking changes in the electronic, thermodynamic and mechanical properties (Thompson 1976). As early as 1927, Herzfeld (1927) noted that the change in conductivity in sodium-ammonia solutions was a direct manifestation of the release of the metal valence electrons following a polarization catastrophe. It is now generally assumed (Edwards and Sienko 1981) that the Mott criterion (5) represents an accurate guide to the *M-NM* transition in these systems. The metallization onset in sodium-ammonia solutions is also responsible for the remarkable liquid-liquid phase separation into metallic (bronze) and non-metallic (blue) constituents at temperatures below ≈ 243 K.

As we have indicated earlier, a true experimental distinction between a metallic and a non-metallic system can only be rigorously applied at $T = 0$ K. This is illustrated in figure 20 which shows 'zero temperature' (specifically 0.003 K) conductivity studies on Si:P. The application of these ideas to the 'hot' sodium-ammonia solutions at 231 K is clearly tantalising but perhaps not as straightforward as at temperatures of a few

* mol % metal = $\left(\frac{\text{moles of metal}}{\text{moles of metal} + \text{moles of NH}_3} \right) \times 100$.

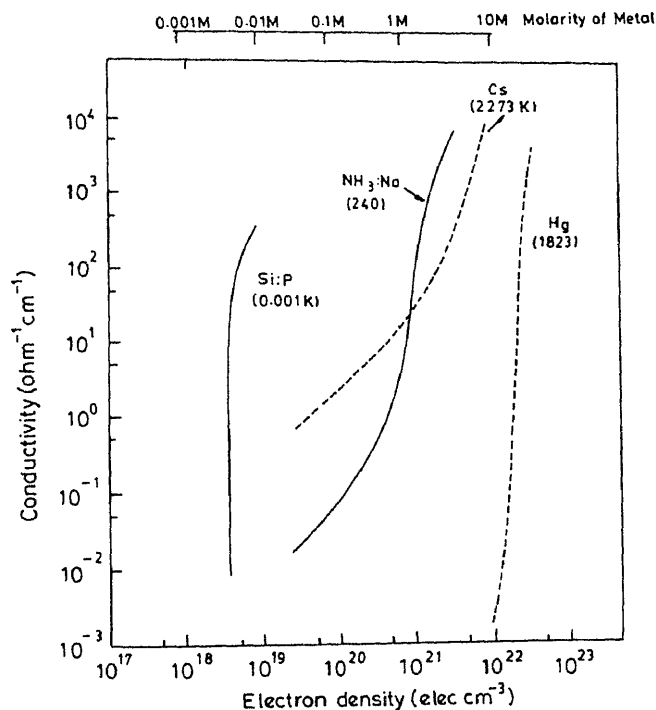


Figure 20. The metal-non-metal transition showing the concentration dependence of the electrical conductivity for a variety of systems. The appropriate observation temperatures are given.

millikelvin. However, note also from figure 20 that although extremely low temperatures generally produce a sharp *M-NM* transition this is by no means a universal feature. The conductivity data for sodium-ammonia solutions (231 K) and expanded mercury (Hensel 1971) at 1823 K show a precipitous drop in conductivities for very small changes in electron density.

8. Metal-metal halide melts

Liquid metal-metal halide mixtures (e.g. Na-NaCl, Cs-CsCl, etc., Hg-HgCl₂, Bi-BiBr₃) form genuine solutions which link the metallic and non-metallic states by a continuous *M-NM* transition at intermediate concentrations (Warren 1981). A number of physical mechanisms for electron localization versus itineracy have been involved which rely on the concepts of Mott, Hubbard and Anderson as applied to liquid state systems. Magnetic susceptibility and magnetic resonance studies (NMR, ESR) have proved to be most informative and direct indicators of how the microscopic electronic structure of both localized and itinerant electron states change across the transition. For example, the nuclear spin relaxation rate is governed by a characteristic time for fluctuations of

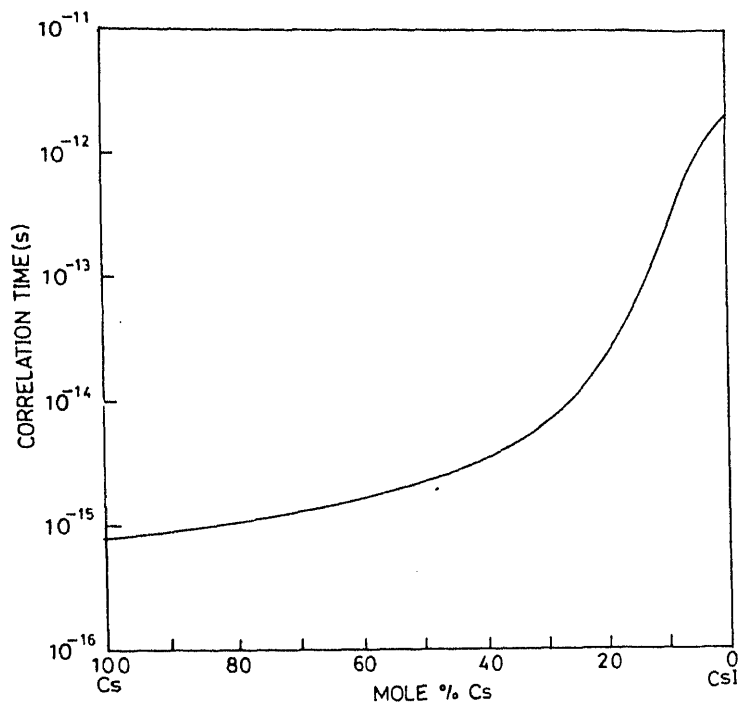


Figure 21. The characteristic NMR correlation time, τ , versus composition for liquid Cs-CsI solutions (Warren and Sotier 1981) at 913 K.

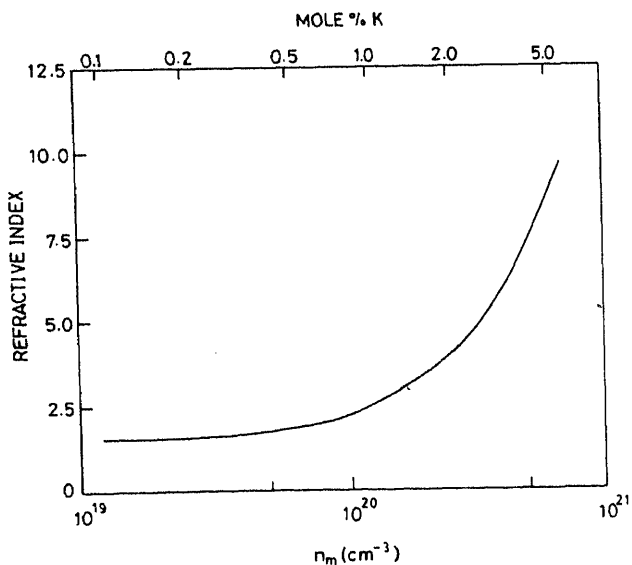


Figure 22. The refractive index vs. excess metal density (n_m) for K-KCl at 1133 K. The upper scale indicates metal concentration in mol % K (Freyland *et al* 1983).

$\approx 10^{-12}$ sec close to the non-metallic limit for which τ is now related to the normal ionic diffusion time (Warren and Sotier 1981).

Another approach for identifying the transition is the polarization catastrophe—the divergence of the refractive index on approaching the M - NM transition from the insulating side. The onset of this effect has been observed by Freyland *et al* (1983) in K/KCl (figure 22). Interestingly, the data show that the dielectric transition occurs at a substantially smaller value of the potassium concentration than either $\sigma_{\min}$ for the solutions or the critical point.

9. Expanded metals

Fluid metals, e.g. Cs, Rb, Hg, expanded to critical conditions offer perhaps the best possibility for an experimental verification of the various types of M - NM transitions in one-component systems (Hensel 1971). Thus, the complexity of the concentration-induced M - NM transition in binary systems (e.g. metal-ammonia, etc.) can be avoided. However, a major technological challenge is posed not only by the very high temperatures and pressures required to bring the sample near its critical density (table 1), but also by the extremely reactive nature of the elements themselves. However, considerable, spectacular progress has been made during the past two decades into the study of the M - NM transition in these expanded systems (Hensel 1984). Recent experiments on metals near their liquid-vapour critical points have shown that there are profound changes in their electronic structure in that region, as evidenced by dielectric anomalies and very rapid changes in electrical conductivity with density (Hensel 1984). Regardless of the precise details of the effective interactions in the limits of localized and itinerant electron regimes, the M - NM transition ensures that these interactions *must* change with density. For example, there is a change from metallic cohesion in the dense liquid to a van der Waals type interaction between neutral atoms (Cs_2 etc.) in the

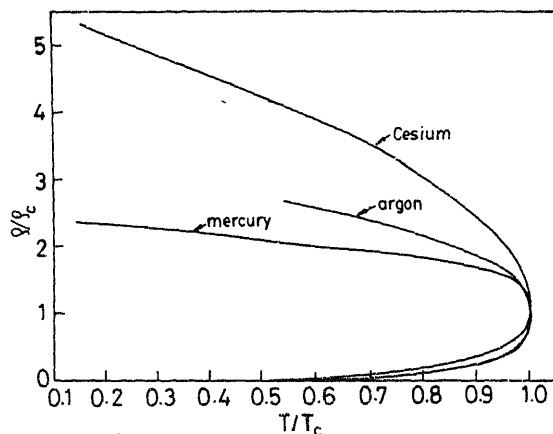


Figure 23. The density variation along the liquid-vapour coexistence curve for metals in comparison with argon (Hensel 1984). The reduced densities P/P_c are plotted versus reduced temperature T/T_c .

dilute vapour. This fundamental difference between the changing interactions taking place in an expanded liquid metal and what one might term a 'normal' fluid, such as argon, are manifest in the form of the liquid-vapour phase behaviour (figure 23). The phase diagram of the metals Hg and Cs have a distinct asymmetry in contrast to the phase behaviour of liquid argon. Thus 'Mott asymmetry' has also been noted for the coexistence curve for phase separation in sodium-ammonia solutions (Thomas 1984).

10. Quasi-one-dimensional conductors

A number of quasi-one-dimensional materials, both organic and inorganic, exhibit high electrical conductivity (Hodine 1984; Subramanyam 1981; Subramanyam and Naik 1984) and a present-day review of metallic materials would be incomplete without a reference to them. The conductivity is anisotropic since the electrons can move more easily in one of the directions. The popularity of this topic is primarily due to the expectation that high temperature superconductivity may be exhibited by them (Little 1964). Metallic and superconducting properties are not found in these materials as commonly because of the lattice distortion (Peierls' transition) that is expected to occur in one-dimensional metals or due to the presence of disorder. Quasi-one-dimensional conductors can be classified under the following categories: (a) organic charge-transfer complexes and salts, (b) conducting polymers and (c) metal-chain compounds. Some of these are depicted in figure 24.

Among the organic metals, the most well known are charge-transfer complexes of the type, tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) and salts such as TTF halides. A number of modifications of TTF-TCNQ including the selenium analogues have been investigated. Conditions for the formation of these metals are roughly the following: (i) the donor and acceptor molecules must be planar both in neutral and ionic states; a slight deviation in planarity could facilitate closer packing; (iii) the complex should form segregated stacks; this happens when the overlap between the donor and acceptor orbitals is not large; (iv) there must be unpaired electrons in the system and partial

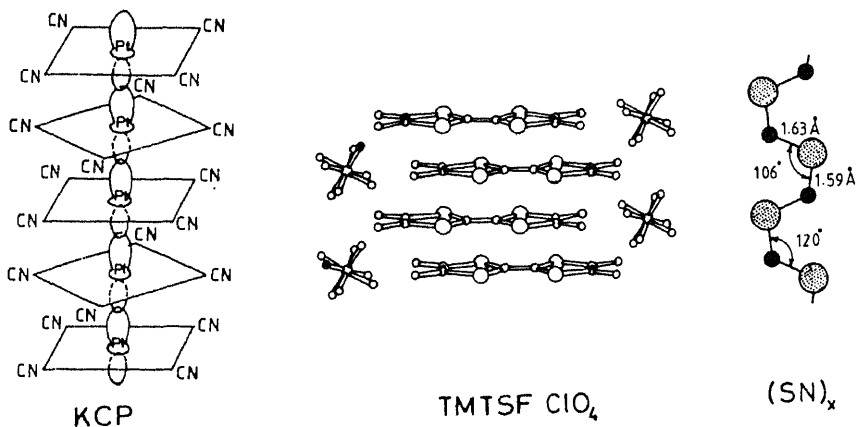


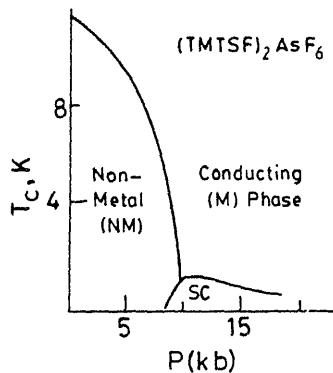
Figure 24. Typical quasi-one-dimensional conductors (see text for full description of the solids).

charge-transfer must occur. Electrical conductivity is low in neutral and ionic complexes; (v) the charge densities should be located near the opposite ends of the molecular unit so that it becomes highly polarizable.

Charge-transfer complexes are generally made up of stacks of donor and acceptor molecules. In single stack systems such as TTF halides and salts of TCNQ, only donor or acceptor molecules form stacks (figure 24). In TTF-TCNQ, the TCNQ stack is involved in conduction while in the corresponding selenium analogue both the donor and acceptor units are involved. Organic metals have resistivities in the range 5×10^{-4} – $10^{-2} \Omega \text{ cm}$. The metallic resistivity persists down to the lowest temperatures in some of the complexes (e.g. HMTSF-TCNQ where HMTSF = hexamethylene-tetraselenofulvalene) while in some others the resistivity goes through a minimum and then becomes semiconducting (e.g. TTF-TCNQ). Superconductivity has been observed in salts of tetramethyltetraselenofulvalene (TMTSF) under pressure; under normal pressure, the salts change from the metallic state to the non-metallic state. Only $(\text{TMTSF})_2\text{ClO}_4$ becomes superconducting at atmospheric pressure. In figure 25 we show the phase diagram of $(\text{TMTSF})_2\text{AsF}_6$ to illustrate the relation between the metallic, superconducting and non-metallic phases (Jerome and Schulz 1982).

Polysulphur nitride $(\text{SN})_x$, is a conducting polymer (figure 20) which becomes superconducting at 0.3 K (Hatfield 1978). Halogenation of $(\text{SN})_x$ increases the conductivity. Polyacetylene (Chien 1984) when suitably doped with electron acceptors or donors exhibits high conductivity (upto $10^3 \Omega^{-1} \text{ cm}^{-1}$); some of the dopants are I, AsF_5 and Na. Electron conduction in polyacetylenes is explained on the basis of free radical states (neutral solitons), or positive and negative solitons (formed by addition of acceptors or donors respectively) as shown in figure 26. Recent studies (Soos and Ramasesha 1983) however indicate that correlation energy is the more important factor in giving rise to the energy gap in $(\text{CH})_x$. Some other examples of conducting polymers are polyparaphylene- AsF_5 , polythienylene- ClO_4 and poly-2,5-diylpyrrole- BF_4 with conductivities in the range 10^2 – $10^3 \Omega^{-1} \text{ cm}^{-1}$.

Many metal chain compounds exhibit anisotropic electrical conductivity. $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ (KCP) which has a Pt-Pt distance close to that in platinum metal (figure 24) shows a *M-NM* transition around 200 K. Similar square planar complexes with Pt, Ir, Rh and Ni chains have been investigated (Krogman 1969; Miller 1982). Some of the metal trichalcogenides (e.g. NbS_3 , TaSe_3) are one-dimensional



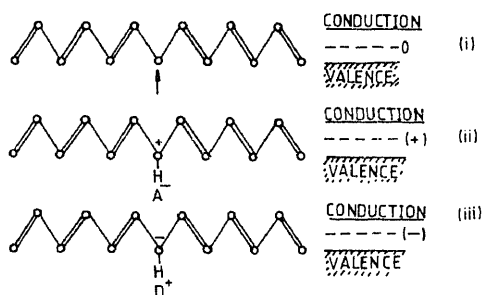
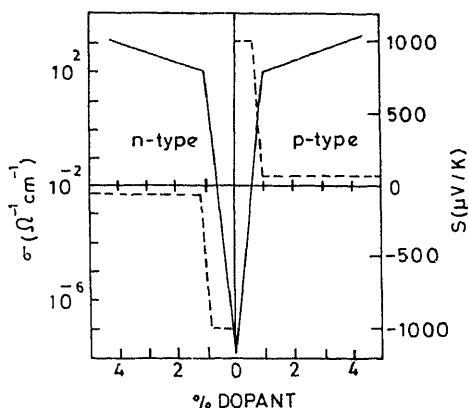


Figure 26. Electrical conductivity and thermopower (S) of doped polyacetylenes (Etemad *et al* 1982), (i) neutral soliton; (ii) positive soliton; (iii) negative soliton.

conductors which become superconducting at low-temperatures. In $\text{Hg}_{2-86}\text{AsF}_6$, orthogonal strands of Hg are present and the ab planes containing these strands exhibit metallic conductivity (Datars *et al* 1978). Other highly conducting systems of interest are organometallic polymers and metalloporphyrins.

11. Concluding remarks

In this article we have attempted to present a brief insight into the important and fundamental question: 'what makes certain materials metallic?'. With this in mind, we have outlined the vast variety of chemical systems which can exist either in metallic or non-metallic states. Our coverage has been primarily representative, but at the same time we have included aspects of both experiment and theory. It is our view that chemists play a cardinal role in the design and manufacture of materials. Our experience has shown that chemists have generally been reluctant to come to grips with—indeed even to recognise—the seemingly strange symbolisms and concepts associated with the physics of itinerant electrons. They are, however, entirely happy with the content, formulation and application of models for localized electrons in liquids and solids. The converse would be applicable to the chemists' view of the

We have identified and exemplified the transition region between the metallic and the non-metallic states of matter. The very fact that such a wide range of chemical substances can transform from a localized (non-metallic) to an itinerant (metallic) electron regime (table 1) seems to suggest that there must exist either a continuous or a discontinuous transition between the disciplines of chemistry and physics. Our hope is that the present article goes at least part of the way in understanding this fascinating transition.

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Nonlinear conduction and electrical switching in one-dimensional conductors

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Abstract. Many one-dimensional conductors show pronounced nonlinear electrical conduction. Some of them show very interesting electrical switching from a low conducting state to a high conducting state. Such electrical switching is often associated with memory. These are discussed with particular emphasis on charge transfer complexes TMBine-TCNQ, TMPD-TCNQ, $\text{Cs}_2(\text{TCNQ})_3$, TEA-(TCNQ)₂ and *o*-tolidine-iodine.

Keywords. One-dimensional conductors; charge transfer complexes; electrical switching; memory phenomena; nonlinear conduction; charge density waves; high pressure phenomena.

1. Introduction

Many charge transfer complexes exhibit interesting properties such as a deviation from ohmic behaviour and switching from a low conducting state to a high conducting state (Subramanyam and Hemamalini Naik 1985). Such behaviour has been observed previously in a wide variety of systems ranging from amorphous chalcogenides like $\text{Te}_{48}\text{As}_{30}\text{Ge}_{10}\text{Si}_{12}$ (Csillag 1973), insulating films of mylar, organic thin films of aromatic hydrocarbons like tetracene, anthracene (Elsharkawi and Kao 1977), polycrystalline thin films of Cu-7,7,8,8-tetracyanoquinodimethane (TCNQ) (Potember *et al* 1979) and chalcogenides like NbSe_3 (Zettl and Gruner 1982).

1.1 Non-ohmic conduction

A deviation from ohmic behaviour at high driving fields has been reported in a number of compounds such as tetrathiofulvalene (TTF)-TCNQ (Gunning and Heeger 1978), quinolinium (TCNQ)₂ (Mihaly *et al* 1979), tetramethyl tetraselenafulvalene (TMTSF)₂PF₆ (Chaikin *et al* 1980) NbSe_3 and TaS_3 (Fleming and Grimes 1979; Miller *et al* 1983) and (CH)_x (Epstein *et al* 1980). Pronounced deviation from ohmicity under applied high pressures at high driving fields has been observed in some organic charge transfer complexes like N,N,N',N'-tetramethyl-*p*-phenylenediamene TMPD-TCNQ, N,N,N',N'-tetramethyl benzidine TMBine-TCNQ (Bandyopadhyay and Subramanyam 1979), $\text{Cs}_2(\text{TCNQ})_3$, triethylammonium TEA-(TCNQ)₂ (Hemamalini Naik and Subramanyam 1984, 1986b; Hemamalini Naik *et al* 1983) and *o*-tolidine-iodine (Hemamalini Naik and Subramanyam 1983b, 1986a; Hemamalini Naik *et al* 1982).

A number of theories have been proposed to fit the experimental data, none of which

corresponds to a situation wherein it is held in a potential varying non-linearity with the displacement from a pinned site. Such systems exhibit nonlinear response to any external perturbation. The nonlinear current-voltage (*i-v*) characteristics in a pinned CDW system can arise from various phenomena such as solitons. The depinning of CDW by zener tunnelling has also been considered (Miller *et al* 1983). The other mechanisms considered are space charge limited currents (Farges *et al* 1972), phonon assisted hopping through random barriers, impurity pinning (Lee and Rice 1979) and sliding CDW (Frohlich 1954).

1.2 Electrical switching and memory phenomena

It is known that the characteristic electrical properties of many materials undergo drastic changes at high fields in excess of 10^6 V cm^{-1} . In insulators, such high fields lead to a destructive breakdown while in some amorphous materials, such effects can be nondestructive. In these cases, the physical processes after breakdown are quite different from those before and are of considerable interest and have been exhaustively studied (Turnbull and Bagley 1975; Klein *et al* 1971; Le Comber and Mort 1973). Nondestructive breakdown is closely related to switching. Both have similar developments leading to a change in the material from a low conducting *OFF* state to a high conducting *ON* state with $\sigma_{\text{ON}}/\sigma_{\text{OFF}} \sim 10^2\text{--}10^4$.

Switching is a result of application of an electric field higher than a threshold onto the specimen. Once the specimen has switched to the *ON* state, it behaves in one of the two ways to an applied bias: it either returns to the *OFF* state once the bias is removed in which case it is called threshold switching, or it remains in the *ON* state even after the applied bias is removed in which case, it is called memory switching. The different properties of the two states find a number of applications (Fritzsche 1973). To study what initiates switching, the dependence of the switching field on parameters such as electrode materials, sample thickness, temperature and pressure must be considered.

The *i-v* characteristics and electrical switching, as a function of high hydrostatic pressure (upto 7 GPa), yield interesting results. A number of charge transfer complexes (1DC) such as TMBine-TCNQ, TMPD-TCNQ, $\text{Cs}_2(\text{TCNQ})_3$, $\text{TEA}(\text{TCNQ})_2$ and *o*-tolidine-iodine have been subjected to such studies.

Various mechanisms of thermal and electronic origin have been considered to explain the switching phenomena. This phenomena is not very well understood. Under pressure, various factors have to be taken into consideration. The pressure dependence of the switching field and activation energy are not very well understood. A comprehensive review of our experimental results in these areas is given here.

2. Experiments

Reversible and rapid bistable switching has been observed in polycrystalline samples of Cu-TCNQ sandwiched between two metal electrodes with switching field less than $3 \times 10^3 \text{ V cm}^{-1}$ (Potember *et al* 1979). The device acts either as a threshold switch or as a memory switch depending on the strength and duration of the applied field. The switching behaviour can be directly related to the reduction potential of the acceptor.

Anthracene thin films sandwiched between metal strips also show threshold switching (Elsharkawi and Kao 1977). After several switching cycles, the switching

anged to a memory type. Switching was observed only in samples less than $5\text{ }\mu\text{m}$ thickness.

In NbSe_3 , threshold switching shows up in direct I - V traces and leads to a hysteresis increasing and decreasing driving currents (Zettl and Gruner 1982) at $T = 26.5\text{ K}$. With increasing temperature, the hysteresis becomes progressively smaller disappearing at $T = 38\text{ K}$ where nonlinear conduction begins.

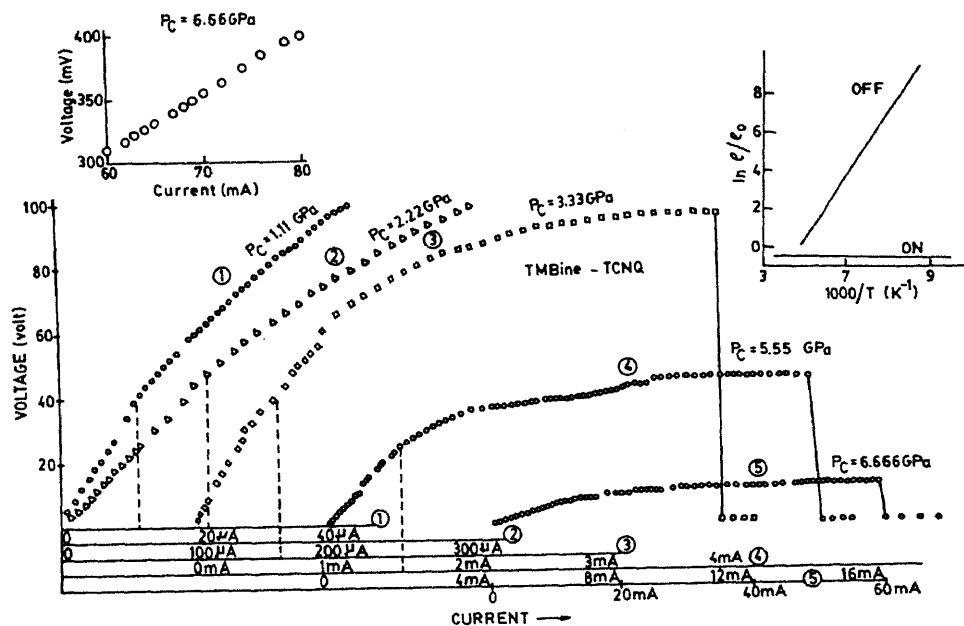
The I - V characteristics have been studied under pressure up to 7 GPa of some charge transfer complexes (figures 1-4). The characteristics show a strong deviation from the ohmic behaviour before switching to the *ON* state. The nonlinearity is more pronounced with increasing pressures. The switching current also increases with an increase in pressure while the switching field decreases (figure 5). The switching field is typically 10^3 V cm^{-1} and $\sigma_{\text{ON}}/\sigma_{\text{OFF}} \sim 10^2$ - 10^4 . The driving force in all these cases is a current source.

In TMbine-TCNQ , the *ON* state can be driven back to the *OFF* state by the application of an a.c. pulse of a suitable frequency and duration. In the case of TMPD-TCNQ , the *OFF* state is restored by warming the sample to about 50°C .

Theory

1 Non-ohmic conduction

Non-ohmic conduction has been exhaustively studied in the linear chain compounds NbSe_3 (Monceau *et al* 1976; Ong and Monceau 1977). Early measurements gave the



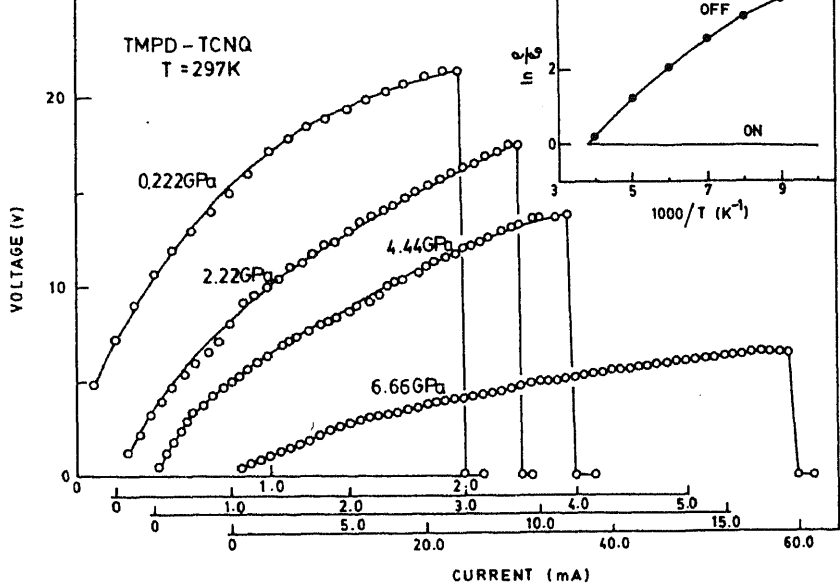


Figure 2. Current-voltage characteristics of TMPD-TCNQ at high pressures. (inset shows $1000/T$ for ON and OFF states).

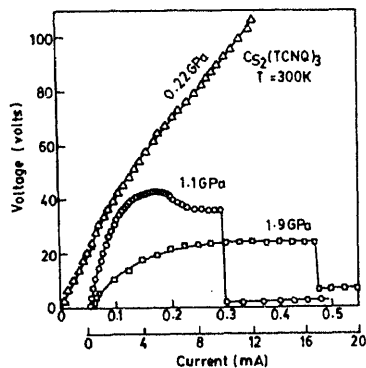


Figure 3. I-V characteristics of $\text{Cs}_2(\text{TCNQ})_3$ at different pressures.

value for the field dependent conductivity as

$$\sigma(F) = \sigma_a + \sigma_b \exp(-F_0/F).$$

The second term on the right hand side is due to the sliding charge density waves. This expression for the field dependent conductivity suggests a zener tunnelling across a pinning gap. Later Brill *et al* (1981) showed that the data could be fitted approximately by a modified tunnelling formula where F is replaced by $F - F_T$ ($F > F_T$), F_T being the threshold field. A revised scaling relation between field and frequency gives good agreement between a.c. and d.c. coupling effects providing strong evidence in favour of

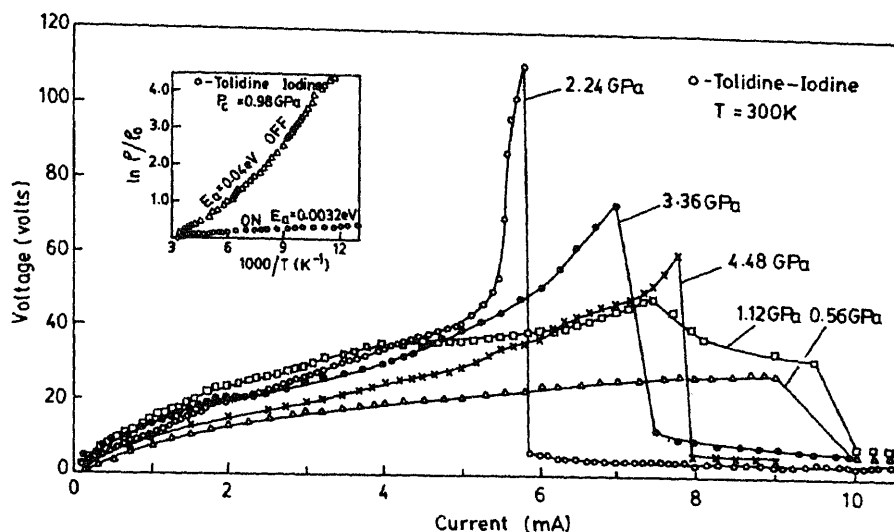


Figure 4. I - V characteristics of o -tolidine-iodine at different pressures.

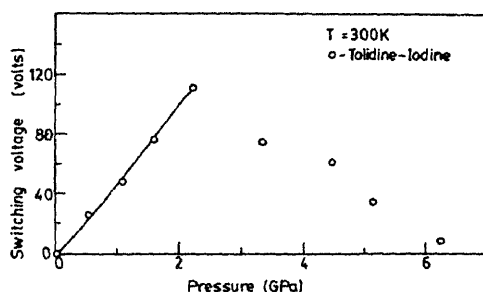


Figure 5. Switching voltage as a function of pressure for o -tolidine-iodine.

the tunnelling interpretation of the CDW dipinning (Miller *et al* 1983). A revised relation of the above tunnelling equation is

$$I_{dc} = G_a F + G_b (F - F_T) \exp(-F_0/F),$$

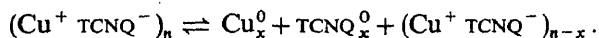
where F_0 is the characteristic field for zener tunnelling. The linear term represents the ohmic conductivity and the second term arises due to the CDW.

Alternatively, the I - V characteristics can also be fitted to an equation of the type

$$I(E) = A(1 - e^{-BE})(e^{CE + DE^2}).$$

electrons. Switching could also be the result of electrode injection or consequences of non-ohmic conduction. In the latter case, one can invoke two models to explain the switching phenomena: depinning of the CDW and tunnelling through the coulomb barrier of charged impurities. Switching observed in NbSe₃ is associated with the CDW state. Dielectric breakdown (O'Dwyer 1973) has also been considered as a possible mechanism. In the presence of an electric field, the electron gains energy, some energy is lost due to collisions with the phonons. If the energy gained exceeds the energy lost, for some electric field, then the energy of the electron can increase indefinitely resulting in breakdown of the system.

Some of the other mechanisms invoked to explain the switching mechanism are the field induced solid state reversible electrochemical reaction associated with the charge transfer salts as in the case of Cu-TCNQ (Potember *et al* 1981; Kamitsos *et al* 1982)



This case has been verified using various spectroscopic techniques.

It was suggested that the switching observed in anthracene thin films was due to the formation of stacks of charge transfer complexes across samples between the electrodes leading to easy charge transfer. This can happen via donor-acceptor interactions which are retained even after the removal of the applied field and broken when an a.c. pulse is applied; although the data available are insufficient to identify it.

4. Discussion

4.1 Non-ohmic conduction

The non-ohmic part of the I - V characteristics of TMPD-TCNQ and TMBine-TCNQ have been fitted to an equation of the type

$$I(F) = A[1 - \exp(-BF)] \exp(CF + DF^2)$$

and the fit is found to be satisfactory.

In the case of TEA-(TCNQ)₂, Cs₂(TCNQ)₃ and *o*-tolidine-iodine, it has been fitted to an equation of the type

$$\sigma(F) = \sigma_a + \sigma_b \exp(-F_0/F).$$

Figure 6 gives a plot of $\ln[\sigma(F) - \sigma_a]$ as a function of $1/F$ of TEA(TCNQ)₂, Cs₂(TCNQ)₃ and *o*-tolidine-iodine respectively. As seen from the figure, the equation gives a good line on fit. Hence, in all these cases, the non-ohmic conductivity has been attributed to the zener tunnelling type of CDW. Though the formation of CDW is questionable at room temperature, the applied pressure plays an important role (Hemamalini Naik and Subramanyam 1984, 1986; Hemamalini Naik *et al* 1983a).

Nonlinear transport has been observed in TTF-TCNQ and related compounds KCP and NbSe₃ (Cohen and Heeger 1977). For the TTF compounds, Lee *et al* (1974) suggested a hopping type motion of the pinned CDW condensate and a resulting field dependent conduction. Cohen and Heeger (1977) suggested a conduction of the type $\sigma = \sigma_0(1 + \beta E^2)$ where β takes into account the defects and impurities. The unambiguous proof for the intrinsic nature of the nonlinear transport came from microwave harmonic mixing.

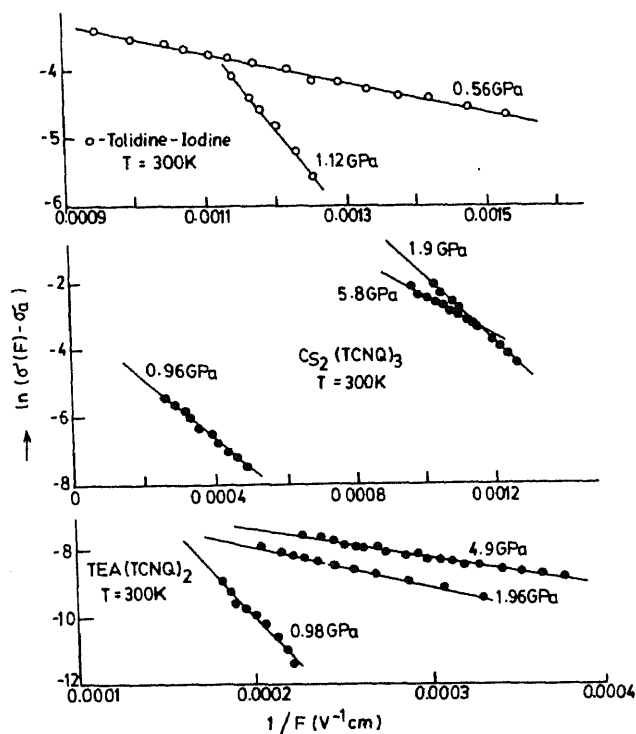


Figure 6. Variation of $\ln [\sigma(F) - \sigma_0]$ of the charge transfer complexes with the inverse of field.

4.2 Electrical switching

Electrical switching has been most extensively studied in amorphous chalcogenides. Here it has been suggested that when the heat generated is greater than the heat lost, an instability occurs whereby the current and the self-heated region collapse to a filament establishing a new stationary state rapidly within a switching time $< 10^{-10} \mu sec$ (The ON state dynamic resistance is 1–10 ohm). Switching characteristics are obtained as solutions to the heat transport and charge conservation equations subject to proper boundary conditions, device geometry, external circuitry and material properties. As long as the current exceeds a minimum or holding current, the system is in its ON state. When the current is reduced, it returns to the OFF state within $1 \mu sec$.

When the switching has been observed under pressure, the various mechanisms considered are dielectric breakdown, zener tunnelling, thermal breakdown etc.

4.2a Dielectric breakdown: Above a critical field, if the electron gains more energy than it loses to the lattice, then its energy increases considerably resulting in the breakdown of the system by the relation

frequency. P depends on the switching power, the sample geometry and the number of electrons/cc.

Calculations done for typical cases show that this mechanism is not responsible for switching in the present experiments.

4.2b Zener tunnelling: The application of pressure reduces the band gap increasing the probability of zener tunnelling from the valence band to the conduction band. An increase in the probability is also enhanced as a result of switching when the activation energy is considerably reduced. We have the probability for such a process

$$P_{v-c} = \exp \left[- (2/3eF) (2m^*/h^2)^{1/2} \Delta^{3/2} \right],$$

where F is the switching field and Δ the activation energy after switching. When substitution is made for various pressures, the probability is found to be negligible. These calculations are not exact, but do indicate that zener tunnelling is not the cause of switching.

4.2c Thermal breakdown: Thermal breakdown can occur when the conductivity has a strong dependence on temperature. The application of an electric field produces Joule heating which increases the temperature which in turn increases the conductivity and hence the current. When the joule heat generated by the current flow is greater than the heat lost by conduction, an instability occurs which drives the system into a new state (Miller *et al* 1983). In all the cases where the charge transfer complexes are studied under pressure, they are firmly embedded in the steatite pressure transmitting medium between the tungsten carbide anvils. Moreover, the *ON* state is not very activated. The total amount of heat supplied to the sample at the time of switching is less than 0.2 watts. Measurements of the temperature of the sample do not show any appreciable increase in temperature during the switching experiment. This amount of heat is distributed over the entire sample and dissipated to its surroundings. Hence thermal runaway has been ruled out as a possible mechanism.

4.2d Electrochemical process: That electrical switching is an electrochemical reaction of the type observed in Cu-TCNQ has been ruled out as the temperature dependence of the conductivity in the two states is quite different from that observed in Cu-TCNQ. Also the complexes are of the donor-acceptor type and not of the metal-salt type.

5. Memory phenomenon

When the *ON* state is maintained even after the driving current is removed, it is called memory switching. Whenever a marked change in properties accompanies a bistable switching, it has device potential, as a memory for information storage. In an electrical memory, the stored information is read out and erased electrically. The two conducting states are both stable at zero electrical bias. For optimum instability, $\rho_{OFF}/\rho_{ON} \sim 10^5$ or less. To produce the memory *ON* state, a critical 'set time' has to be exceeded

6. Conclusions

Detailed experiments on the d.c. conductivity of organic quasi one-dimensional conductors at high pressures have clearly demonstrated pronounced nonlinear conduction and electrical switching. The nonlinear conduction is explained on the zener tunnelling model. Electrical switching is associated with memory effects. Dielectric breakdown, thermal breakdown and zener tunnelling are not responsible for switching. The electrical switching observed is attributed to some collective electronic excitations in the complex.

Acknowledgements

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Electron-electron interactions in polyacetylene†

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Abstract. Experimental evidence for strong electron-electron interactions in polyacetylene is presented. These include (i) observation of a dipole forbidden state below the optical gap, (ii) observation of negative spin densities at sites at which noninteracting models predict zero spin density (iii) vanishing optical gap, in the infinite chain limit, in the closely related symmetrical linear cyanine dyes. To correctly explain these features it is necessary to solve correlated model Hamiltonians. Using diagrammatic valence bond method model exact solutions of correlated models of finite-size systems can be obtained and various physical properties of the low-lying states can be computed. These properties, when extrapolated to the infinite chain limit explain many of the experimental features observed in polyacetylene.

Keywords. Electron correlation; valence bond method; polyacetylene; optical gap; spin densities.

1. Introduction

Chemists have long been interested in polyenes, both from experimental and theoretical standpoints. For instance, it was known from extrapolations of experimental data on optical gaps of finite polyenes that an infinite polyene should have a finite optical gap of ~ 2.25 eV (Murrell 1963). There was also much interest concerning the bond alternation in infinite polyenes, since in finite systems, aromatic molecules like benzene had equal C–C bond lengths while linear chain molecules like hexatriene had alternating short and long C–C bonds. While Coulson (1938) predicted uniform bond lengths for infinite polyenes, Kuhn (1948) predicted dimerization of the carbon chain to account for the finite optical gap. Later calculations by Longuet-Higgins and Salem (1959) showed that the ground state energy per carbon atom varied as $\delta^2 \ln |\delta|$, for small δ , where δ is the alternation in the transfer integral. Because of this logarithmic dependence of the ground state energy on the bond alternation, it is to be expected that the ground state is always dimerized, independent of the stiffness of the carbon chain or the strength of electron-lattice coupling constant. This also follows from a more general argument put forth by Peierls (1955) which leads to the conclusion that partially filled one-dimensional bands in the ground state are unstable with respect to a $2k_F$ distortion of the lattice. Polyacetylene, being a half-filled one-dimensional band should undergo a Peierls dimerization in the ground state. Experimentally, x-ray (Fincher *et al* 1982) and NMR (Yannoni and Clarke 1983) investigations have, in fact, conclusively demonstrated bond alternation of 0.03 ± 0.01 Å in polyacetylene.

are located in the middle of the optical gap. Neutral solitons possess spin while charged solitons are nonmagnetic. Electron spin resonance studies on undoped all-trans polyacetylene have indeed shown the presence of paramagnetic defects (Goldberg *et al* 1979). However, firm evidence for midgap absorption in all-trans polyacetylene is lacking.

All the theories of polyacetylene mentioned above start from the Hückel limit. Electron-lattice interaction leading to alternation in the Hückel transfer or resonance integral is introduced along with a static strain energy contribution. Electron-electron interactions have been considered to be very weak and either neglected or included only in a perturbative scheme (Kivelson and Heim 1982). However, there is considerable experimental evidence in favour of strong electron-electron interactions in polyacetylene. The importance of electron correlations in polyenes has been stressed among others by Cizek *et al* (1969), Ovchinnikov *et al* (1972), Honig *et al* (1975) and Matsen (1978).

It has long been known from extrapolations of experimental data that the optical gap in symmetrical cyanine dyes vanishes in the limit of infinite chain length (Brooker *et al* 1945). This is rather puzzling since symmetrical cyanine dyes differ from polyenes only in the end groups and in the limit of infinite chain length this difference should be negligible (Platt 1956). Hence, attributing the optical gap in polyenes entirely to bond alternation is incorrect. The Hückel based models also fail to explain the existence of optically forbidden states below the optical gap in polyenes with four or more double bonds (Hudson *et al* 1982; Ohmine *et al* 1978). The observed oscillator strength for the transition across the optical gap is smaller, by at least a factor of two, than that predicted by the Hückel theory (Salem 1966). Recent ESR studies (Thomann *et al* 1983) have shown the presence of negative spin densities in polyacetylene radicals on sites where the Hückel theory predicts zero spin density. These experimental results clearly bring out the inadequacy of Hückel type models and show the importance of electron-electron interactions in polyacetylene.

Besides explaining the above experimental results, introduction of electron-electron interactions should not result in a uniform ground state as this would contradict the x-ray and NMR results on polyacetylene. For this reason, an investigation of the effect of electron-electron interactions on Peierls dimerization also becomes necessary.

Some of the theoretical methods employed for studying correlated models are the Hartree-Fock (HF) and unrestricted Hartree-Fock (UHF) methods, perturbation methods, quantum renormalization group methods, and extrapolations from exact diagonalization of finite systems. The HF method gives qualitatively the same results as the Hückel model and hence is not suited to explain many of the features discussed above. While the UHF theory is better, it suffers from the drawback that the method does not conserve total spin and consequently predicts spin density wave states even in singlets (Fukutome and Sasai 1982). Perturbation methods work when the correlations are weak and we will demonstrate that the correlations in polyacetylene are strong thereby rendering perturbation method unsuitable in these systems. The quantum renormalization group method (Chui and Bray 1978) is also not accurate since it confines to a rather small part of the Hilbert space spanned by the Hamiltonian. Finite system calculations offer a viable alternative provided reasonably large systems can be solved exactly. Since in the minimum basis Hamiltonian, there are 4^N possible states for every site, the basis set increases with the system size N as 4^N . To be able to deal with large systems (large N) the full symmetry of the Hamiltonian should be exploited. The

correlated model Hamiltonians conserve total spin (S_{tot}) besides S_{tot}^Z . Therefore, valence bond (vb) functions which are eigen functions of S_{tot} as well as S_{tot}^Z are the natural choice of basis for finite system calculations.

2. VB method for finite model Hamiltonians

The Hamiltonian employed for modelling polyacetylene is the Pariser-Parr-Pople (PPP) Hamiltonian given by

$$H = H_t + H_{\text{corr}}.$$

$$H_t = \sum_{p,\sigma} t_p (a_{p,\sigma}^* a_{p+1,\sigma} + a_{p+1,\sigma}^* a_{p,\sigma}),$$

$$H_{\text{corr}} = U \sum_p \hat{n}_p (\hat{n}_p - 1)/2 + \sum_{p > p'} V_{pp'} (\hat{n}_p - 1) (\hat{n}_{p'} - 1), \quad (1)$$

where $a_{p,\sigma}^*$ ($a_{p,\sigma}$) creates (annihilates) an electron with spin σ in the orbital at site p . The transfer integral t_p is estimated to be 2.4 ± 0.17 eV for double and single bonds for polyacetylene. U is the on-site correlation energy which from gas phase ionization and electron affinity data for carbon is 11.26 eV. Since polyacetylene chains are semi-conducting, the screening of correlations is not very effective and long-range interactions will also have to be included besides the on-site interactions U . The second term in H_{corr} corresponds to such interactions and is given by the Ohno formula (Ohno 1964)

$$V_{pp'} = U(1 + 0.6117 r_{pp'}^2)^{-1/2}, \quad (2)$$

which interpolates between U for $p = p'$ and $\pm(e^2/r_{pp'})$ for $|p - p'| \rightarrow \infty$. The Hamiltonian with only on-site interactions is also useful in these studies, since for uniform t_p , the model has been exactly solved for the infinite chain (Lieb and Wu 1968) and provides a stringent test of extrapolations. Since we are interested in comparing results between correlated and uncorrelated models for the same lattice stiffness and electron-lattice interactions, we have not considered the elastic term.

A normalized singlet vb function can be generated by operating on the vacuum state with $a_{pa}^* a_{pb}^*$ for a doubly occupied site p and by $(a_{pa}^* a_{qb}^* - a_{pb}^* a_{qa}^*)/\sqrt{2}$ for singlet pairing of electrons on sites p and q . A given vb function can be conveniently represented as a diagram with dots ($\cdot$) at empty sites, crosses ($\times$) at doubly occupied sites and lines between pairs of sites at which electrons are singlet paired (figure 1). These diagrams in turn can be coded in the binary system by associating two bits per site (Ramasesha and Soos 1984a). The states of the bits are '00' for any empty site, '10' for a site at which a line begins, '01' for a site at which a line ends and '11' for a site that is doubly occupied. The Rumer-Pauling rule states that linear independence and completeness can be achieved by retaining all diagrams without intersecting lines, on arranging the N sites at the vertices of a polygon. This rule makes the binary representation of a vb diagram unique.

All the vb diagrams with a given total spin S , a given number of sites N and a given number of electrons N_e on the N sites can now be generated in an increasing sequence of integers that represent them, by simply examining whether the bit patterns of

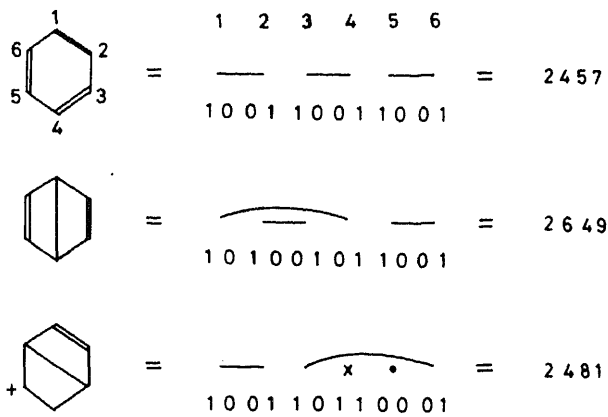


Figure 1. Typical singlet vB diagrams for six electrons on six sites and their bit representation.

integer in question corresponds to a vB diagram of the given characteristics. The total number $P_s(2n, N)$ with spin S , $N_e = 2n \leq N$ is given by

$$P_s(2n, N) = \frac{2S+1}{N+1} \frac{[(N+1)!]^2}{(n+S+1)!(n-S)!} \times \frac{1}{(N-n-S)!(N+S+1-n)!} \quad (3)$$

$P_s(2n, N)$ is much smaller (usually by a factor of $\sim 3-4$) than the complete basis formed by Slater determinants. The size of the basis can further be reduced by taking into account electron-hole and spatial symmetries that may exist in the Hamiltonian.

The vB basis is diagonal in the correlation part of the Hamiltonian (1) but is off-diagonal in the transfer part. The exact matrix representing the model Hamiltonian can be obtained by operating on the vB functions by the Hamiltonian (Mazumdar and Soos 1979). The matrix elements are defined by

$$H|k\rangle = \sum_j h_{kj}|j\rangle, \quad (4)$$

where $|i\rangle$ represents a vB function. Determining the column index in h_{kj} is made efficient since the vB diagrams are arranged as increasing integers that allow binary searching. The Hamiltonian matrix $\mathbf{h}$ is non-symmetric, because the vB basis is non-orthogonal. As with any configuration interaction calculations, the matrix $\mathbf{h}$ is sparse. We are interested only in a few low-lying states, so that taking advantage of the sparseness, it is possible to deal with upto $\sim 60\,000 \times 60\,000$ matrices on a supermini computer like VAX 11/780. The low-lying eigen values and corresponding eigen vectors are obtained by coordinate relaxation and deflation where necessary (Ramasesha and Soos 1984a).

Calculation of matrix elements between correlated states first requires that the correlated state be normalized, i.e., we need to evaluate

$$R = \sum_{k,k'} C_{k'n} C_{kn} S_{k,k'}. \quad (5)$$

$S_{k'k}$ is very time consuming. On the other hand, using charge orthogonality of vb functions, the basis can be rearranged such that $S_{k'k}$ is block diagonal with blocks of the same size being identical (figure 2) (Ramasesha and Soos 1984b). We are now left with the simpler task of evaluating the overlap matrix elements within a block and that too only once for a block of a given size. The overlap matrix elements are calculated using Pauling's island counting scheme (Pauling 1933). For instance, for a 10 electrons on 10 sites problem, the singlet basis has 19 404 diagrams. The overlap matrix of this basis when written in the block-diagonal form has one 42×42 block and several 14×14 , 5×5 , 2×2 and 1×1 blocks. The overlap matrix is calculated only once for the 14×14 , 5×5 and 2×2 blocks even though they appear several times.

Matrix element calculation for operators diagonal in the vb representation is straightforward. An example of such an operator is the dipole moment operator. The transition dipole between eigen states $|\psi_n\rangle$ and $|\psi_m\rangle$ of the Hamiltonian (1) is given by

$$M_{nm} = \frac{1}{R} \langle \psi_n | \mu | \psi_m \rangle = \frac{1}{R} \sum_{k,k'} C_{k'm} C_{kn} \mu_k S_{k'k}. \quad (6)$$

The matrix elements of operators which are not diagonal in the vb representation but conserve total spin can also be calculated easily. However, in such calculations the resultant state obtained by the effect of such operators on the eigen state of the Hamiltonian requires reordering into the block-diagonal sequence. An example of such an operator is the operator for obtaining bond orders,

$$b_p = \sum_{\sigma} (a_{p+1,\sigma}^* a_{p,\sigma} + a_{p,\sigma}^* a_{p+1,\sigma}). \quad (7)$$

Matrix elements of operators that do not conserve total spin and also do not transfer electrons between sites such as the local spin density operator s_p^z , the spin-spin

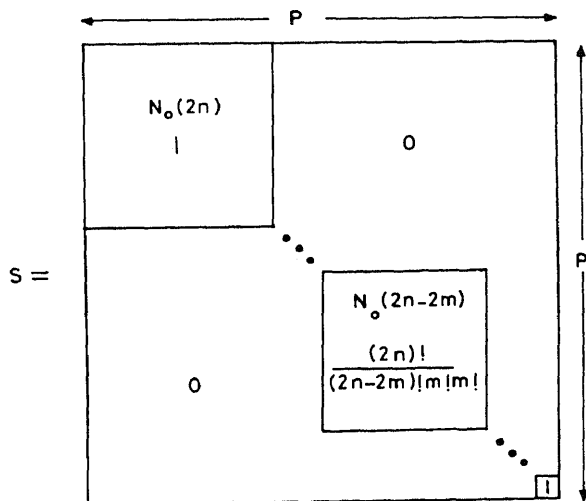


Figure 2. Overlap matrix S in the block-diagonal representation. $N_0(2r)$ are the covalent singlets for $2r$ electrons on $2r$ sites. The expression below $N_0(2r)$ gives the number of times a

correlation operator $s_p^z s_q^z$ can also be handled in this scheme by more general techniques (Ramasesha and Soos 1985).

Evaluation of such a variety of matrix elements between model exact eigen states of Hamiltonians helps in a better comparison of the model with a wide range of experimental results that exist for polyacetylene.

3. Results and discussion

Our method of obtaining results for the infinite chain is based on extrapolation of the model exact finite system results to the infinite limit. Although it is known that complete configuration interaction calculation is size consistent, there is no *a priori* theoretical basis for extrapolations. Therefore, to have confidence in the extrapolation procedures, it is necessary that we compare the extrapolated results with exact infinite chain results, wherever they exist. Fortunately, in the present case, exact ground state energy per site as well as the optical gap of infinite uniform Hubbard chains ($V_{pp'} = 0$ for $p \neq p'$) is known (Lieb and Wu 1968). Since $U = 4t$ in the Hubbard model is the most difficult regime in the parameter space for approximate methods, we compare our extrapolated results for this case with the exact results for the ground state energy per site (figure 3) as well as the optical gap (figure 4). The extrapolated value for the ground state energy per site is -0.573 ± 0.005 while the exact result is -0.57373 , in units of t . The optical gap from extrapolations is 1.20 ± 0.1 while the exact gap is 1.2867 , again in units of t . These

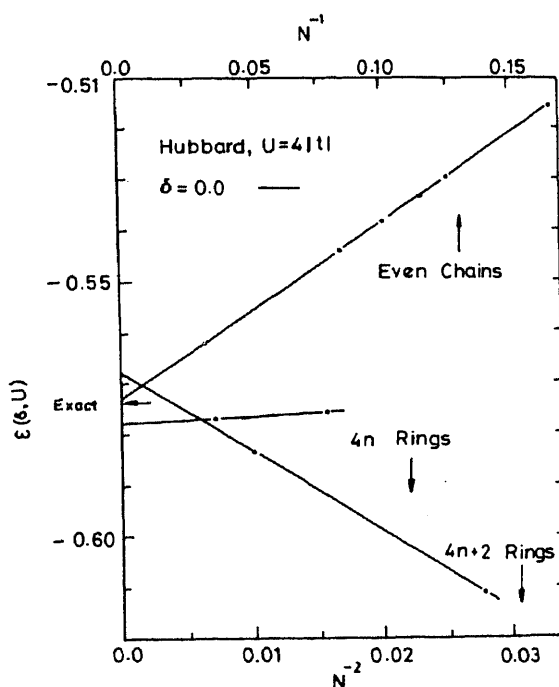


Figure 3. Ground state energy per site $\epsilon(0, U)$ in units of t for the uniform Hubbard model, vs N^{-1} for chains and N^{-2} for rings.

results, besides giving confidence in the extrapolation methods also show that in such schemes, ground state energy per site has smaller error than the optical gap. This is important since in studying the effect of correlations on dimerization of the half-filled one-dimensional band, we would be comparing the difference in ground state energies per site between $\delta = 0$ and $\delta \neq 0$ cases, which are rather small for small δ .

Although exact results do not exist for $\delta \neq 0$ case of the Hubbard model, our results show that the optical gap widens by ~ 0.20 (in units of t), in clear disagreement with the meanfield result (Bychkov *et al* 1966) which predicts the gap to widen by only 0.03 (in units of t) on introducing this dimerization. This once again illustrates that the predictions of mean field theory should be viewed with caution.

In the case of the full Hamiltonian of (1), there are no known exact results for the infinite system. However, we can compare exact results for finite chains with experimental quantities since finite chains correspond to small polyenes. Using the same values of U , t and δ , we find our results for all-trans $N = 8$ and $N = 10$ chains to be in very good agreement with the spectroscopic data for octatetraene and decapentaene (table 1). The optical gaps in pentadienyl and heptatrienyl ions from the theory are 3.456 eV and 2.79 eV while experiments yield a gap of 3.42 ± 0.12 eV and 2.88 ± 0.04 eV respectively. The correlation diagram in figure 5 shows that the correlations split the degenerate excited states in the Hückel model. States with electron-hole symmetry in which covalent vb diagrams appear with nonzero coefficients are lowered relative to the states with opposite electron-hole symmetry in which the covalent diagrams have strictly zero weight. In the limit of very large correlations, all the

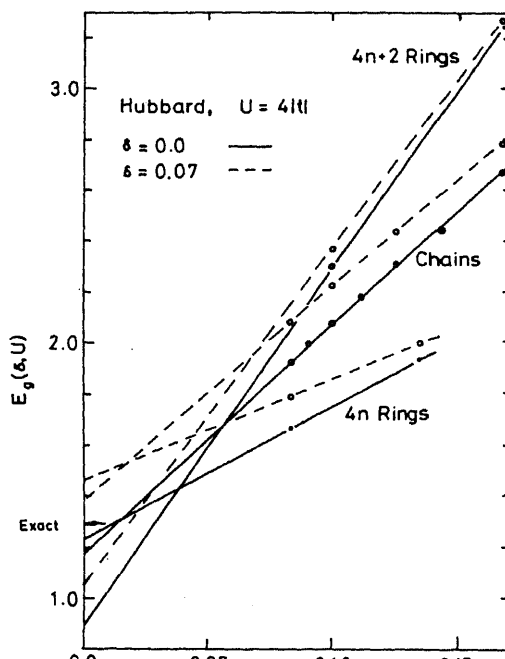


Table 1*. Exact PPP and experimental excitation energies of all-trans ($N = N_g = 8$) and decapentaene ($N = N_g = 10$). Covalent and ionic labels of electron-hole symmetry. The lowest dipole-allowed excitation is underlined.

State		Decapentaene		Octatetraene	
$S = 0$	$S = 1$	PPP (eV)	Experimental (eV)	PPP (eV)	Experimental (eV)
1^1A_g (cov)		—	—	—	—
	1^3B_u (cov)	1.756	—	1.920	—
	1^3A_g (cov)	2.566	—	2.929	—
	2^3B_u (cov)	3.388	—	3.844	—
2^1A_g (cov)		3.404	3.10	3.775	—
1^1B_u (cov)		4.210	—	4.718	—
1^1B_u (ion)		<u>4.234</u>	<u>4.02</u>	<u>4.561</u>	—
2^1B_u (cov)		5.323	—	6.644	—
	1^3A_g (ion)	5.494	—	5.977	—
1^1A_g (ion)		5.589	—	6.086	—
	1^3B_u (ion)	6.458	—	7.072	—

* From Ramasesha and Soos (1984b); cov = covalent; ion = ionic.

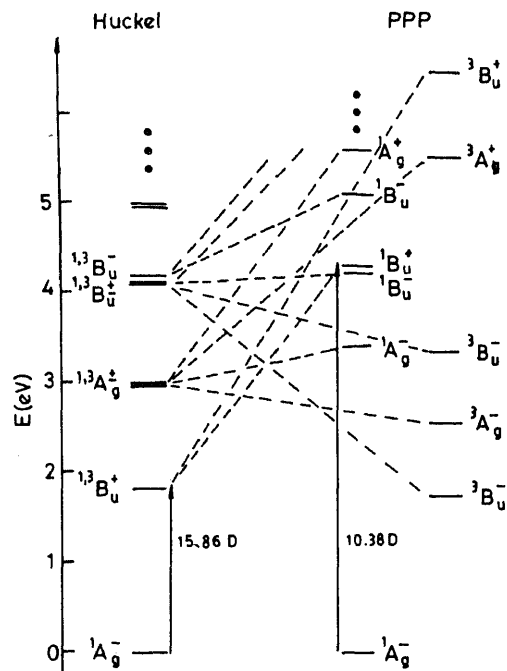


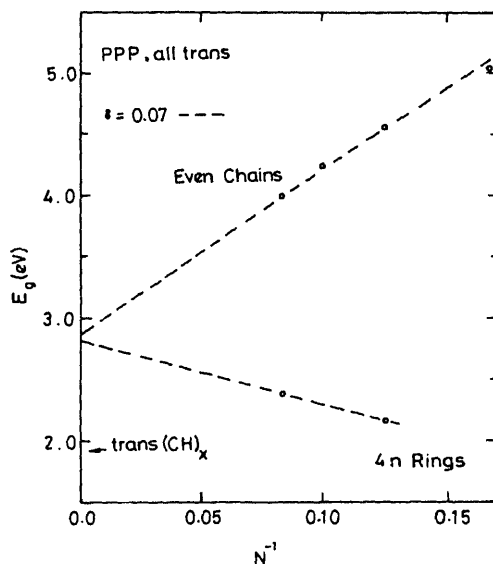
Figure 5. Correlation of Hückel and PPP excitation energies for all-trans decapentaene with alternation $\delta = 0.07$, also shown is the theoretical transition moment for the transition.

covalent states descend below the optical gap and form spin-wave excitations of the chain. Figure 5 shows that for decapentaene, with our parameters, there exist two optically forbidden states below the optical gap. Existence of the $2A_g^1$ state in decapentaene is experimentally confirmed from gas phase optical studies and is located 3.10 eV above the ground state, to be compared with the model exact value of 3.404 eV. Figure 5 also indicates that the transition moment for the lowest optical transition is lowered substantially from the Hückel value and is in much better agreement with experiments (Soos and Ramasesha 1983a). It appears that our parameters slightly overestimate the correlations. Nonetheless, our calculations convincingly prove that correlations are very strong in polyacetylene and cannot be neglected or even included reliably within a perturbative scheme.

The extrapolations from finite-size system to the infinite system has been done for both rings and chains (Soos and Ramasesha 1984). Ideally, the ring and chain extrapolations for $N \rightarrow \infty$ should give the same values. However, because of small system sizes the two extrapolations do not converge to the same value. The mismatch in these extrapolations gives an estimate of the error involved in these procedures.

Figure 6 shows the extrapolated optical gap for a single strand of polyacetylene. The $\delta = 0$ extrapolation is also indicated on the figure to show that most of the optical gap arises from electron correlations rather than from dimerization. The extrapolated gap of 2.8 ± 0.2 eV should be compared with the observed solid state gap of 1.9 eV. Considering that the gas phase optical gap will be red shifted by ~ 0.5 eV in the solid state, we find that the correlations we have assumed slightly overestimate the correlations in polyacetylene.

It is well known that correlations introduce negative spin densities on sites where the HF theory predicts zero spin density (McConnel and Chesnut 1957). Indeed, as already mentioned, negative spin densities have been observed in radicals of all-trans



polyacetylene (Thomann *et al* 1983). In figure 7, we have plotted the ratio of total negative to positive spin density, calculated from the correlated ground state wave function, versus inverse system size (Soos and Ramasesha 1983b). The same ratio calculated for uniform Heisenberg chains with odd numbers of spins is shown to delineate the large U limit. Experimentally observed ratios for polyacetylene radicals with $N \sim 50$ is also shown. The comparison between the theoretical and experimental results once again confirms our view that we have only slightly overestimated the correlations in polyene chains.

Figure 8 shows the dependence on system size of optical gaps of uniform chains, ions with odd numbers of carbon atoms and cyanine dyes, as well as of covalent gaps of radicals. The optical gaps of uniform chains fall on the same line for both even and odd chains. This shows that the mid-gap state does not exist in the correlated models. This is to be expected since the optical gap is primarily due to correlations and only weakly dependent on dimerization. Cyanine dyes are similar to ions of the carbon chain with odd number of carbon atoms and show vanishing optical gap in the finite chain limit. In both the systems, in the infinite chain limit the ground and optically excited states can be described as incommensurate charge density waves shifted in phase and therefore they have the same energy. The covalent gap also vanishes for uniform chains, consistent with the result for uniform Heisenberg chains where the ground state singlet and lowest excited singlet are degenerate to $O(1/N)$ (Ramasesha and Soos 1983).

Effect of correlations on the dimerization of one-dimensional half-filled bands has been of considerable interest. Qualitative arguments based on the concept of resonance put forth by Mazumdar and Dixit (1983, 1984) leads to the conclusion that on-site correlations tend to stabilize the dimerized state. This is borne out by their calculations on rings of six and ten carbon atoms. Mazumdar and Campbell (1985) have extended this argument to long-range coulomb interactions. Soos and Ramasesha (1984) have compared the stabilization of the infinite dimerized chain in the presence of both on-site and extended range interactions, obtained from extrapolations of exact results for

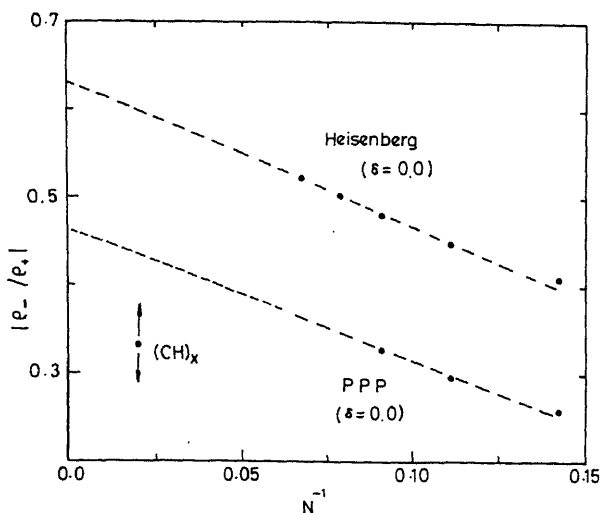


Figure 7. Absolute ratio of total negative to positive spin density vs N^{-1} for Heisenberg spin chains and the PPP Hamiltonian. $(CH)_x$ value is from Thomann *et al* (1983).

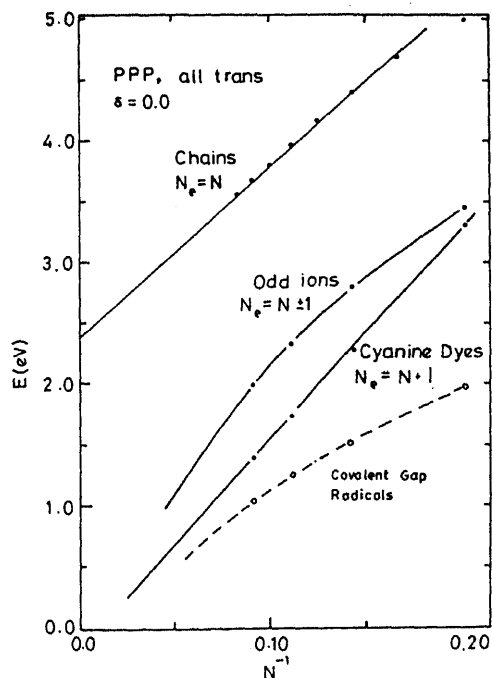


Figure 8. Optical gaps vs N^{-1} of uniform PPP chains, ions of odd segments and linear cyanine dyes. The covalent gap of radicals is dipole forbidden.

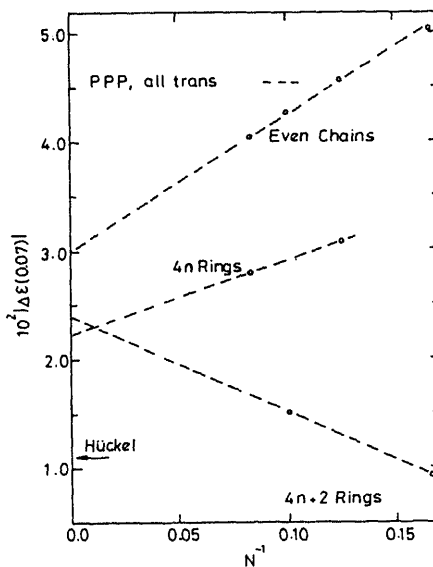


Figure 9. $\Delta \epsilon(\delta) = \epsilon(\delta) - \epsilon(0)$ where $\epsilon(\delta)$ is the ground state energy per site for alternation δ in the PPP model, vs N^{-1} . Hückel value for the infinite chain is indicated by the arrow.

both rings and chains of upto twelve carbon atoms, with the stabilization in the Hückel model (figure 9). It is seen that correlations indeed stabilize dimerization. Therefore existence of correlations is consistent with both the observed dimerization and the other experimental results already discussed. However, what remains to be included in a more complete theory of polyacetylene is the interchain interactions and effects of dopants. Further work in this direction is currently in progress.

The diagrammatic *vs* method together with bit representation provides a powerful technique for exact diagonalization of diverse types of finite model Hamiltonians. It can also be used together with different types of approximation schemes such as Lanczo's scheme (Roomany *et al* 1980) or the quantum Monte Carlo method (Hirsch *et al* 1982). Work in these directions is in progress. However, the success of finite system calculations in predicting the properties of infinite systems may not be as dramatic as in the simple case of polyacetylene unless reliable scaling methods are developed for quantum systems.

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On some aspects of metallisation with special reference to iron group transition metal oxides

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Abstract. The metal-insulator transition in 3d transition metal oxides such as the ternary perovskite oxides as well as the binary oxides both as a function of composition and temperature are reviewed. The description of metallisation in terms of a change in sign of the temperature coefficient of resistance as well as conductivity at 0 K are considered in terms of modern theories based on localisation. It is pointed out that there may be grounds to believe that in the high temperature limit a resistivity less than $\approx 10^{-1}$ ohm cm may be associated with metallic properties despite a negative temperature coefficient of resistance. The correlation between magnetic and electrical properties have also been examined.

Keywords. Metallisation; 3d transition metal oxides; localisation.

1. Introduction

Several inorganic and organic compounds are known to exhibit metallic behaviour (Rao and Edwards 1986, for a brief review of such systems). The interest is to examine whether there are common features associated with metallisation in these systems. The classical requirement for metallic behaviour has been a positive temperature coefficient of resistance (TCR) as distinct from semiconductors which show a negative TCR. The composition controlled metal-insulator transition is then thought to be signalled by a change in the sign of TCR as a function of composition. However, in as much as semiconductor is considered to exhibit activated transport behaviour an insulator would be one which exhibits zero conductivity at 0 K (σ_0). A metal would then be one which shows a finite σ_0 . In the latter case there may exist situations where the TCR is actually negative as discussed recently (Mott 1985, Mott and Kaveh 1985). By this definition the concept of metal-insulator (MI) transition has become blurred and there are several problems that are yet to be understood.

In this article we shall discuss the metallisation in oxides with special reference to the oxides of the iron group transition metals. The small radial extension of the 3d electrons makes the bonding mainly ionic so that the bandwidths are expected to be narrow. The electrical transport and magnetic properties are considered to be due to electrons of predominantly 3d character. A strong correlation between magnetic and electrical properties is therefore anticipated. We shall examine both the composition-controlled and temperature-induced MI transition from the viewpoint of recent experimental and theoretical work.

2. Universal characteristics

Mott (1967, 1972, 1985b) had quite early proposed a theory for the existence of a minimum metallic conductivity, $\sigma_{\min}$, using the theory of localisation proposed by Anderson (1958). According to this theory, the high-temperature intercept of the $\log \sigma$ vs $1/T$ plot of compositions which are insulating would correspond to the value of $\sigma_{\min}$ which is given by

$$\sigma_{\min} = (1/3)g^2e^2/\hbar a \simeq 0.03 e^2/\hbar a \quad (1)$$

where $g \sim (1/3)$ and a is the separation between charge carriers. The change in sign of TCR occurs around the value of $\sigma < \sigma_{\min}$. The situation envisaged by Mott is shown in figure 1. The concept of $\sigma_{\min}$ is based on the assumption that the mean free path l cannot be less than the interatomic spacing a . Without disorder this can be shown (Ioffe and Regel 1960) to be nearly equal to $(1/3)e^2/\hbar a$. The factor g in (1) is introduced to account for disorder, as a decrease in the density of states (N_E) at E_F is expected over that without disorder (N_E^0), with $g = (N_E)/(N_E^0)$. In concentrated systems $a \sim 2\text{--}4 \text{ \AA}$ and $\sigma_{\min} \sim 200\text{--}500 \text{ ohm}^{-1} \text{ cm}^{-1}$. One of the early predictions of Mott was that σ_0 would drop discontinuously to zero through a composition-controlled MI transition when σ becomes less than $\sigma_{\min}$. At low temperatures the insulating compositions are presumed to show in this model variable range hopping (Mott 1969) with $\sigma \propto \exp(-A/T^{1/4})$ for three-dimensional systems.

Recently, however, scaling theories (Abrahams *et al* 1979, 1980; Ramakrishnan 1985; Lee and Ramakrishnan 1985) have shown that $\sigma_{\min}$ does not exist in the sense that there is no discontinuous decrease of σ_0 to zero. In this theory a dimensionless conductance $G(L)$ is defined for a cube of side L [$G(L) = (Lh/e^2)\sigma(L)$]. A function $\beta(G)$ can then be defined such that $\beta(G) = d \ln G(L)/d \ln L$. This function is shown to be a universal function of G only. In three dimensions β has a zero at a value G_c . Then G is a constant G_c in the neighbourhood of zero and this should be an universal constant. Thus

$$\sigma = (e^2/\hbar) G_c/L. \quad (2)$$

The above equation leads to a vanishing conductivity as L tends to infinity. This contradicts the predictions of Mott. In the Anderson (1958) model, Mott had argued that for a limiting value of V/B , (where $\pm \frac{1}{2}V$ are the limits of the random potential well

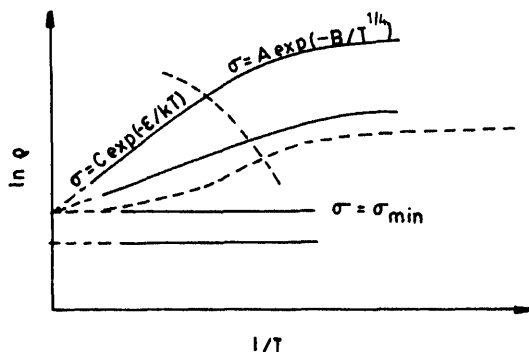


Figure 1. Expected changes in resistivity as a function of composition during a

and B is a bandwidth) all states are localised upto a limiting energy called the mobility edge. As V/B increases the density of states at E_F till at the limiting value it approaches the value g in (1). Thus the conductivity at the mobility edge in Mott's model is given by (1). Equation 2, however, shows that at the mobility edge g vanishes so that there can be no minimum metallic conductivity. Physically, this is due to an effect called 'incipient localisation' arising out of quantum interference effects (Bergmann 1983) of the two paths that an electron can have under time reversal symmetry. This backward scattering causes an electron diffusing out of a point to return to the original point thus adding to localisation effects.

Mott has proposed that at finite temperatures

$$\sigma_{\min} = 0.03e^2/\hbar L_i \quad (3)$$

where L_i is the distance that an electron diffuses before suffering an inelastic collision. According to Mott and Kaveh (1985) eq. (3) is the limiting value of the conductivity as the localisation length, increases, since the conductivity would be determined by the value of L_i rather than ξ which is the distance in which the wave functions are little changed. L_i is assumed to decrease with increasing temperature and approaches the value a at high temperatures so that in the high temperature limit (1) is recovered. The exact temperature dependence of L_i is not known. Mott and Kaveh (1985) have proposed that L_i varies as $1/T$ when electron-electron collisions are involved.

Most of Mott's arguments are based on the band picture. When V/B is greater than the limiting value the localised states reside within the band tails. These localised charges carry current through phonon-assisted hopping. In an alternate model for charge conduction polarons are sometimes postulated (Emin 1983). In this model the atoms in the vicinity of a charge carrier are displaced to produce a potential well in which the charge carrier is self-trapped. When only a few atoms are involved these are called small polarons, the spatial extent of the charge carrier being small. The small polaron is favoured as the residence time of a charge carrier at a site increases. Small polaron bands have very narrow band widths. The formation and electronic transport properties of these polarons have been discussed recently by Emin (1983). The description of electrical transport in these systems is based on the Einstein relation $\sigma = ne^2 D/kT$ where D is the diffusion constant ($= a^2 \nu$) with $\nu = \nu_0 \exp(-E_a/kT)$. In the limit of the activation energy $E_a = 0$ the maximum conductivity for small polaron hopping is expected to be around $10^1 \text{ ohm}^{-1} \text{ cm}^{-1}$ (Frohlich 1954; Bosman and van Daal 1970). It is to be noted that the ionic conductivity in superionic conductors has an upper limit close to the value of $1-10 \text{ ohm}^{-1} \text{ cm}^{-1}$. This value of the conductivity is restricted by the attempt frequency, ν , which is of the order of 10^{12} sec^{-1} , the phonon frequency. The attempt frequency, ν , may be related to the exchange integral J through $J = h\nu$ as proposed by Zener (1951) and Zener and Heikes (1953), Zener obtains an expression for the conductivity as

$$\begin{aligned} \sigma &\simeq (ne^2 J a^2 / \hbar kT) \exp(-E_a/kT) \\ &\simeq e^2 J / \hbar a kT, \end{aligned} \quad (4)$$

when $E_a = 0$, $\nu = J/h$ and $n = (1/a^3)$. Equation 4 gave a close estimate of the value of the conductivity for several double exchange systems. It is interesting to note that when J is of the order of kT , (4) gives the Ioffe-Regel (IR) limit, $\sigma_{\text{IR}} (\simeq e^2/3 \hbar a)$. Zener's derivation would seem to imply that the attempt frequency in (4) can be related to the

The composition-controlled MI transition in oxides from the viewpoint of $\sigma_{\min}$ were first examined in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ and $\text{Ln}_{1-x}\text{Sr}_x\text{VO}_3$ (Mott 1972; Rao *et al* 1977; Rao and Om Parkash 1977). In these systems disorder is created by a random distribution of Sr^{2+} and the disordering potential is the difference in the charge potential. The MI transition is considered to be due to delocalisation of Co^{4+} or V^{4+} holes which are bound to Sr^{2+} for small values of x . Predictions based on the Anderson model were substantiated by the observation of a linear $\log \rho$ vs $T^{-1/4}$ plot at low temperatures. The value of the conductivity at which TCR changes sign is around $500 \text{ ohm}^{-1} \text{ cm}^{-1}$. These observations were consistent with the postulates of Mott. The intriguing feature is the nearly universal value of the critical composition x_c ($\approx 0.28 \pm 0.03$) at which TCR changes sign. In $\text{La}_{1-x}\text{K}_x\text{VO}_3$ (Bazov *et al* 1982) $x_c \approx 0.13$ which seems to indicate that the critical parameter is the percentage of B^{4+} ions.

The MI transition in the $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$ system ($B = \text{Cr, Mn, Fe, Co}$) have been studied recently (Ganguly *et al* 1984). LaNiO_3 is metallic while the LaBO_3 compounds are magnetic insulators (see Goodenough 1972). The Ni^{3+} and B^{3+} ions have the same charge but are likely to have different $3d^n$ energies. Any disorder is therefore likely to arise from changes in the exchange potential. In these systems also, it is observed that TCR changes sign around the value of $\sigma \sim 500 \text{ ohm}^{-1} \text{ cm}^{-1}$. Localisation effects are most pronounced with Mn^{3+} and Cr^{3+} . An examination of the energy level diagrams of Mizushima *et al* (1979) for the $3d^n$ metal ions in TiO_2 shows that Mn^{3+} and Cr^{3+} ions are furthest energetically from that of Ni^{3+} . This could account for their strong localising influence (see Rao and Ganguly 1985a, 1985b). Several other systems such as $\text{LaRu}_{1-x}\text{B}_x\text{O}_3$ ($B = \text{Ga, Fe}$) show changes in the sign of TCR around $\sigma \sim 300\text{--}500 \text{ ohm}^{-1} \text{ cm}^{-1}$ (Bouchard *et al* 1973, 1977).

The compositions with x close to x_c and with negative TCR could nevertheless be metallic in the sense of a finite $\sigma(0)$. There are several indicators to this behaviour:

(i) We have observed (Ganguly *et al* 1984) that the conductivity in the $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$ systems in the range 15–300 K could be fitted to an empirical expression of the type

$$\sigma = A \exp \left[-E_a/k(T + \theta) \right], \quad (5)$$

where θ is positive and A approaches $\sigma_{\min}$ as x approaches x_c . A finite value of θ implies a finite σ_0 . The above fit has been subsequently found to be successful in several other oxide systems. Extension of resistivity studies down to lower temperatures is under way to examine the existence of σ_0 as well the validity of (5).

(ii) An infra-red study in the range $1000\text{--}300 \text{ cm}^{-1}$ of $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$ showed (Ganguly and Vasanthacharya 1986) that features due to localised optic modes disappear when the resistivity of the system decreases below $\sim 10^{-1} \text{ ohm cm}$. This is about two orders of magnitude more than the value corresponding to $\sigma_{\min}$ (1) or the value at which TCR changes sign. Such behaviour has been observed in several other perovskite and layered perovskite oxide systems with the K_2NiF_4 structure.

(iii) In the $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ system the $x = 0.05$ and 0.10 compositions show nearly temperature-independent resistivity below 40 K although at higher temperatures they show a negative TCR. This would imply a finite σ_0 . These systems show anomalous magnetic susceptibility behaviour below 40 K (Vasanthacharya *et al* 1984a). This behaviour has been associated with itinerant electron behaviour as the more insulating $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ system does not show such behaviour although Co-O-Mn interac-

compositions in the $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ systems show a resistivity at low temperatures $\sim 10^{-1}$ ohm cm while in the corresponding $\text{LaCo}_{1-x}\text{Mn}_x\text{O}_3$ system $P > 10^4$ ohm cm.

4. Temperature induced metal-insulator transition

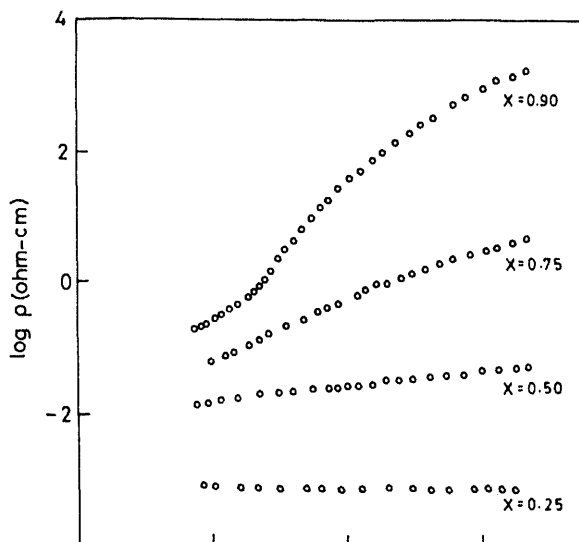
For pure compounds where there is no disorder the concept of localisation or $\sigma_{\min}$ is not really applicable. Many of the 3d transition metal oxides such as CrO_2 , TiO , SrCrO_3 , SrFeO_3 , LaNiO_3 etc., which are metallic, have resistivities in the range 10^{-3} – 10^{-4} ohm cm at ordinary temperatures (see Rao and Rao 1970 and references therein). However, compounds such as LaCoO_3 , LaTiO_3 , $\text{La}_2\text{NiO}_{4+\delta}$, La_2CuO_4 etc., (Goodenough 1972, Rao and Rao 1970, Rao and Ganguly 1985a, 1985b, and references therein) which are considered to be metallic at high temperatures with positive TCR, are semiconducting with a negative TCR at lower temperatures. In these compounds, the value of the resistivity at higher temperatures is greater than that ($\sim 2000 \mu$ ohm cm) corresponding to $\sigma_{\min}$ in disordered systems. Like the Mooij criterion applicable to amorphous metals (Mooij 1973) a criterion for the oxides as well as for other compounds (Rao and Ganguly 1986) may be put forward, i.e., there is a limiting value of the resistivity ($\sim 2000 \mu$ ohm cm) for compounds which delineates materials which exhibit a positive TCR from those which exhibit a negative TCR in the absence of a structural distortion. In the case of amorphous metals the limiting value is $\sim 200 \mu$ ohm cm.

The question arises as to what the values of the conductivity at which metallisation is observed are on treating temperature as a disordering field. Some of the most dramatic changes in the resistivity in the temperature-induced MI transitions are shown by 3d transition metal oxides especially the oxides of vanadium and titanium such as VO_2 , $\text{V}_n\text{O}_{2n-1}$, $\text{Ti}_n\text{O}_{2n-1}$. In these oxides the metallic phase has a conductivity of the order of 10^3 ohm $^{-1}$ cm $^{-1}$ which is just larger than the value of $\sigma_{\min}$ expected for these compounds from (1). On the other hand, in Fe_3O_4 the resistivity after the Verwey transition is of the order of 10^{-2} ohm cm which is less than the value of $\sigma_{\min}$ expected. In this compound, the resistivity shows a negative TCR after the Verwey transition until the magnetic ordering temperature above which it is nearly temperature-independent (Miles *et al* 1957). The conductivity at this temperature is around 200 ohm $^{-1}$ cm $^{-1}$ (see Aragon *et al* 1985 and references therein). Thus the high temperature metallisation of materials seems to show that there could be a limiting value of the conductivity for metallisation.

The very careful experimental work on single crystals of $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ and $\text{Fe}_3\text{O}_{4-\delta}$ (Kuwamoto *et al* 1980; Aragon *et al* 1985 and references therein). In the $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ system it is known that the $x = 0$ composition shows a sharp MI transition at 150 K the conductivity in the metallic phase being around 1000 ohm $^{-1}$ cm $^{-1}$. As x is increased the MI transition temperature (T_{MI}) increases. The resistivity in the metallic regime is also increased. At still higher values of x there is a temperature $T_{\text{IM}} (> T_{\text{MI}})$ at which there is a sharp increase in resistivity by several orders of magnitude when $T > T_{\text{IM}}$ the material is semiconducting. This temperature T_{IM} is decreased as x is further increased so that the range of metallic behaviour $T_{\text{IM}} > T > T_{\text{MI}}$ decreases with increase in x and disappears above a particular value x_c . These transitions have been treated in an elegant manner recently by Honig and coworkers (see Honig and Spalek 1986) employing

essentially a Brinkmann-Rice (1970) model and taking into account the free energy contributions from the spin. This study makes a serious and significant contribution to the understanding of temperature induced MI transitions. What is of interest to us is that the re-entrant metallic behaviour is most marked when the resistivity in the metallic phase is close to $\sigma_{\min}$ of (1) and that the metallic phase is not seen when the resistivity in the region $T_{\text{MI}} < T < T_{\text{IM}}$ becomes greater than $\sim 10^{-1}$ ohm cm. Thus the results of the $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ system seem to show that metallicity at high temperatures may be defined when ρ is less than or equal to 10^{-1} ohm cm. In the $\text{Fe}_3\text{O}_{4-\delta}$ system the Verwey transition is first order with a finite enthalpy of transition (see Honig 1986), for small values of δ . The magnitude of the resistivity change at the first order transition (corresponding to the Verwey transition) decreases as δ is increased. The resistivity after the transition is less than 10^{-1} ohm cm. At higher values of δ the transition becomes second order. Interestingly, this happens as the value of the resistivity in the high temperature phase becomes more than $\sim 10^{-1}$ ohm cm. Thus a value of 10^{-1} ohm cm seems to be important at least at high temperatures. In the $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{BO}_3$ systems referred to earlier there are also indications that at high temperatures the resistivity behaviour is not as predicted by Mott (Figure 1) but instead tends to become temperature independent before it reaches the value of the resistivity corresponding to the high-temperature intercept. This is seen for example in the high temperature resistivity studies on $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ in figure 2 (Vasanthacharya 1985) and for the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples (Rao and Om Parkash 1977). The resistivity behaviour in figure 2 is closer to that predicted from the percolation edge model.

In two-dimensional oxides with K_2NiF_4 structure it has been observed that in several systems such as $\text{LaSrNi}_{1-x}\text{Fe}_x\text{O}_4$, $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$, $\text{LaSrNi}_{1-x}\text{Al}_x\text{O}_4$ (Singh 1982; Ganguly 1986) the high temperature intercepts of the $\log \rho$ vs $1/T$ plots extrapolate to a



value of $\sigma \sim 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ so that the high temperature $\sigma_{\min}$ seems to be reduced over that of the corresponding three-dimensional perovskites. In the $(\text{LaO})_{n+1}(\text{LaNiO}_3)_n$ systems it was observed that $n = 2$ and $n = 3$ compositions had a nearly temperature-independent resistivity of $\sim 5 \times 10^{-2} \text{ ohm cm}$ and $\sim 10^{-2} \text{ ohm cm}$, respectively. These results are not consistent with the value of $\sigma_{\min}$ of (1) but it does suggest that metallicity at high temperatures may be associated with resistivities less than 10^{-1} ohm cm .

5. Changes in magnetic properties across metal-insulator transitions

Systems which show a sharp MI transition at elevated temperatures such as V_2O_3 (see Honig 1985) show marked changes in the magnetic susceptibility at the transition. In the composition-controlled metal-insulator transitions the correlation between magnetic and electrical properties are not obvious. In the $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ system compositions with negative TCR show evidence for antiferromagnetic ordering in terms of a maximum in the susceptibility (Dougier and Hagenmuller 1975). The compositions with positive TCR show nearly temperature-independent susceptibility at high temperatures. At lower temperatures there is an enhancement in the susceptibility. The behaviour is similar to that of LaNiO_3 (Vasanthacharya *et al* 1984). The magnitude of the temperature-independent susceptibility is very large ($\sim 700 \times 10^{-6} \text{ emu/mole}$). If attributed to Pauli paramagnetism such a high value would indicate Fermi temperatures around 500–1000 K only or band widths of the order of only 0.1 eV. In LaRuO_3 there is a strong temperature-dependence of the susceptibility (Bouchard *et al* 1973). Indeed in $\text{LaRu}_{1-x}\text{Ga}_x\text{O}_3$ there is hardly any change in the nature of the high temperature susceptibility especially in the slopes of the χ^{-1} vs T plots for all values of x . Similar behaviour has been found in the $\text{LaNi}_{1-x}\text{Al}_x\text{O}_3$ system for small values of x . In $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$, samples with x close to x_c seem to show evidence for temperature-independence of susceptibility (Vasanthacharya *et al* 1984). These samples have a resistivity less than 10^{-1} ohm cm at the lowest temperatures. Interestingly, we note that the ρ vs $\log T$ plots of some of these samples are nearly linear (figure 3).

It does seem, therefore, that magnetic susceptibility is not clearly correlated with electrical transport properties. Indeed in systems such as LaSrNiO_4 the magnetic susceptibility behaviour is very similar to that of LaNiO_3 at high temperatures. Such similarities in the magnetic susceptibility behaviour in two-dimensional and three-dimensional perovskites have been noticed (Singh 1982; Ganguly 1986). However, despite similar magnetic behaviour the resistivities of the two-dimensional systems are orders of magnitude higher than the corresponding metallic three-dimensional perovskites (Ganguly and Rao 1984; Ganguly 1986). Such behaviour is not anticipated if the magnetic d electrons are also considered to be charge carriers since in the tight-binding approximation the band width is related to the transfer integral which also determines the magnetic properties.

6. General remarks

In several diverse systems such as doped polyacetylene, amorphous Ge-Fe alloys, Na_xWO_3 bronzes etc. the temperature coefficient of resistivity changes sign around the

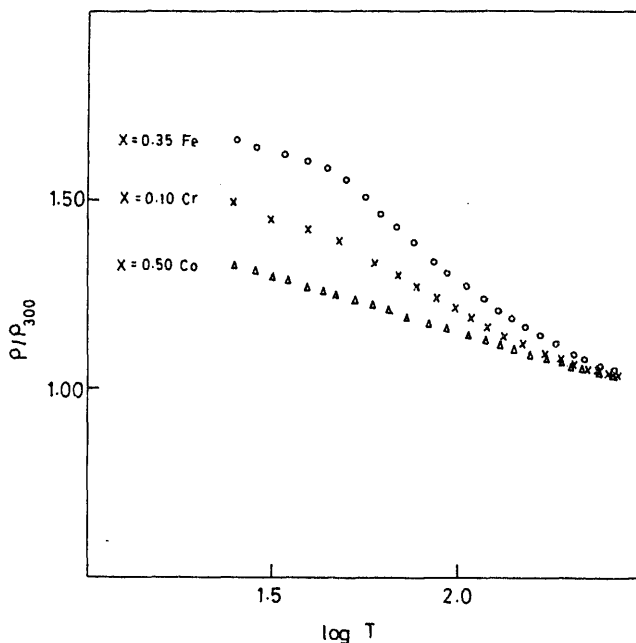


Figure 3. ρ vs $\log T$ plots of some $\text{LaNi}_{1-x}\text{B}_x\text{O}_3$ for values of x close to x_c where TCR changes sign (from N Y Vasanthacharya, unpublished results).

value predicted by (1). The value associated with $\sigma_{\min}$ is thus insensitive to the details of the crystal-field, spin magnitude, crystallinity etc. and thus seems to indicate a universal criterion. Equation 3 has the property of satisfying some of these results both in the high temperature and low temperature limits. At the same time materials with resistivities between $\sim 10^{-1}$ and $\sim 10^{-3}$ ohm cm would seem to be associated with metallic rather than localised electron behaviour despite a negative TCR. The negative TCR is due to the change in L_i . Mott and Kaveh (1985) have proposed that for electron scattering L_i varies as $1/T$. The results in figure 3 would seem to suggest that it is dL_i/dT which varies as $1/T$. On the other hand, since a linear ρ vs $\log T$ plot is reminiscent of the Kondo effect one could argue that a Kondo type of bound state formation leads to an increase in resistivity with decreasing temperature. However, the Kondo mechanism is not properly understood for such poorly conducting systems.

In a qualitative sense the limits of $\sim 10^{-1}$ ohm cm as the minimum activated resistivity and $\sim 10^{-3}$ ohm cm as the maximum metallic conductivity (with positive TCR) may be understood from residence time arguments. It was shown earlier (Rao and Ganguly 1985a, b) that by proposing a minimum relaxation time $\tau_{\min} \sim 10^{-14}$ sec we may obtain a value of $\sigma_{\min}$ from the Boltzmann formula

$$\sigma = ne^2\tau/m^*,$$

close to that predicted from (1) assuming $m^* = 10m_0 \cdot n/m^*$ may therefore be taken as the fraction of charge carriers. $1/f$ noise studies (Prasad *et al* 1979) on $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ have shown that in the metallic state the fraction of charge carriers is around 10%. From Mott's criterion $n_c^{1/3}a_H \sim 0.25$ for metallisation (n_c is the critical charge carrier

concentration per unit volume and a_H is the Bohr radius) the fraction of the volume occupied by the charge carriers with a radius a_H is $\sim 10\%$ of the total volume available from close-packing considerations. In concentrated systems therefore only ten % of the charge carriers need be ionised for Mott's criterion to be satisfied. Interestingly, if we define an effective radius a_{eff} such that $(4/3)\pi n_c a_{\text{eff}}^3 = 0.74$ (the close-packed volume) then $a_{\text{eff}}/a_H = 2.15$ which is close to the ratio of the van der Waals radius of hydrogen atom and its Bohr radius.

An effective mass $m^* \approx 10 m_0$ corresponds to a band width of 0.1 eV which is the value that we obtained from the temperature-independent part of the susceptibility of LaNiO_3 and $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$. From the uncertainty principle, such a band width corresponds to a residence time of $\sim 10^{-14}$ sec. Since this residence time is much less than a typical vibrational period of 10^{-12} to 10^{-13} sec a $\tau_{\text{res}} \sim 10^{-14}$ sec could define a free electron. This would justify the use of a $\tau_{\text{min}} \sim 10^{-14}$ sec in (6). With this definition of τ_{min} for metallicity a metallic conductivity of $\sim 10 \text{ ohm}^{-1} \text{ cm}^{-1}$ would correspond to an effective mass $m^* \sim 1000 m_0$ and a corresponding $\tau_{\text{res}} \sim 10^{-12}$ sec which is just the limit expected for metallisation. NMR experiments (see Warren 1985) on metallisation in liquids support the localisation time scales discussed above.

That a minimum bandwidth corresponding to a minimum τ_{res} may be responsible for metallisation is also seen from the recent observation (Rao and Ganguly 1986) that for liquid elements a heat of vapourisation, ΔH_v , of ~ 0.4 eV per mole distinguishes metallic liquids from the non-metallic ones. This simple criterion cannot of course be applied to all liquids. This also breaks down for elements such as halogens or chalcogens if the dissociation energy, D , is added to ΔH_v of the dimeric molecules in order to obtain the ΔH_v of the element as distinct from the molecule. Apparently, the critical factor seems to be the critical ratio of $\Delta H_v/D$ (~ 1.6) for metallisation to occur.

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Ionic conduction in dispersed solid-electrolytes†

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Abstract. In recent years, considerable interest has been focussed on developing solid electrolytes with high ionic conductivities. One of the latest techniques is the dispersion of a non-conducting and chemically non-interacting phase in the solid electrolyte. These electrolytes have been referred to as dispersed solid-electrolyte systems. The present paper briefly reviews the characteristic features of dispersed solid-electrolytes and the mode of ion conduction in these systems.

Keywords. Ionic conduction; solid-electrolytes; dispersed solid-electrolyte systems.

1. Introduction

One of the reasons for developing solid electrolytes is the need to minimize irreversible losses arising from the high internal resistances in traditional electrochemical devices with aqueous electrolytes. The reduction of internal resistances will assist in the attainment of high reaction rates and good transport conditions. One obvious way to reduce these resistances would be to operate the electrochemical devices at high temperatures. This, however, necessitates the use of ceramic materials having suitably high specific conductivities for ions which can take part in electrochemical processes. The development of such materials, called fast ion-conductors, has contributed to a breakthrough in electrochemical technology. In the literature (Rickert 1982), substantial amount of research and development work has been reported to achieve industrially viable fast ion-conductors. Starting from the discovery of high ionic conductivity in α -AgI (Strock 1934, 1935) during the 1930s, Ag_3SI (Reuter and Hardel 1961, 1965), RbAg_4I_5 (Bradley and Greene 1966, 1967; Owens and Argue 1967) and β -alumina (Weber and Kummer 1967) in the 60s, Nasicons (Goodenough *et al* 1976) and Lisicons (Hong 1978) in the 1970s, the present day endeavours are in developing dispersed solid-electrolyte systems, wherein an ionically conducting matrix is dispersed with a chemically non-interacting and electrically non-conducting phase. Such solid electrolyte systems have been reported to exhibit significantly higher ionic conductivities in relation to pure host solid electrolytes. The present paper highlights some important facets of these solid-electrolytes.

2. Historical background

The development of dispersed solid-electrolytes could be linked to the observation made during the beginning of this century (Jander 1929) that the conductivity of two-

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phase mixtures may exceed the conductivities of pure constituents. In the Wagner (1972) and Crosbie (1977, 1978) studied the conductivity behaviour of semiconductors, with small inclusions of another non conducting phase, which were found to exceed the conductivities of the pure constituents. It is only recently this approach has been extended to solid electrolytes in order to bring enhancements in their ionic conductivities.

3. Characteristic features

Most of the work reported in the literature has been done with the dispersed insulators such as Al_2O_3 , SiO_2 , fly ash, CeO_2 etc., in ionic conductors. The first system, $\text{LiI-Al}_2\text{O}_3$, with a maximum in ionic conductivity for 40 mol % of Al_2O_3 has been reported by Liang (1973). Following Liang, enhancements in ionic conductivity of dispersed solid electrolytes viz., $\text{CuCl-Al}_2\text{O}_3$ (Jow and Wagner 1979), $\text{AgI-Al}_2\text{O}_3$, AgI-SiO_2 , AgI-fly ash (Shah and Wagner 1981a, b, 1982a, b, Wagner 1980), Al_2O_3 (Khandhar and Wagner 1983, Maier 1985a), AgCl-SiO_2 (Maier 1985a), Al_2O_3 (Pack 1979) have been studied. Recently, Fujitsu *et al* (1985) have observed the behaviour in $\text{CaF}_2\text{-Al}_2\text{O}_3$ and $\text{BaF}_2\text{-Al}_2\text{O}_3$ systems, with the maximum in ionic conductivities lying between 10 to 40 mole % of the dispersoid (see table 1).

Vaidehi *et al* (1986), have observed larger enhancement in ionic conductivity with 4 mol % of dispersoid in $\text{CaF}_2\text{-Al}_2\text{O}_3$ and $\text{CaF}_2\text{-CeO}_2$ systems, these compositions have not been studied by Fujitsu *et al* (1985). The enhancement in ionic conductivities between 10^{-4} to $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ for most of these dispersed solid electrolyte systems is evident from figure 1. All these mixtures have been found to be biphasic from x-ray diffraction studies, also the electronic component of conductivity in these materials is nearly negligible (Liang 1973, Jow and Wagner 1979, Vaidehi *et al* 1986).

Table 1. Some characteristics of solid electrolytes containing a variety of dispersed phases.

Material	Dispersoid and its size (μm)	Dispersoid concentration for maximum enhancement ¹	Temperature (K)	Order of enhancement in ionic conductivity
AgI	Dried Al_2O_3 (0.06)	30 m.o	298	50
AgI	Hydrated Al_2O_3	30 m.o	298	10^3
AgI	SiO_2 (0.07)	10 m.o	298	45 (Shah and Wagner 1981)
AgI	Flyash	13.5 w.o	298	51
LiI	Al_2O_3	40 m.o	298	< 50 (Liang 1973)
CuCl	Al_2O_3 (0.06)	10 m.o	333	< 50 (Jow and Wagner 1979)
HgI ₂	Al_2O_3 (0.06)	30 m.o	476	< 10^2 (Pack 1979)
AgCl	Al_2O_3 (0.3)	13 v.o	294	< 10^2 (Maier 1985a)
AgCl	SiO_2 (0.007)	10 v.o	294	< 10^2 (Maier 1985a)
CaF_2	Al_2O_3 (0.02)	2 m.o	663	< 10^2 (Vaidehi <i>et al</i> 1985)
CaF_2	CeO_2 (0.01)	2 m.o	663	< 10^3 (Vaidehi <i>et al</i> 1985)
BaF_2	Al_2O_3 (0.3)	20 m.o	773	< 20 (Fujitsu <i>et al</i> 1985)
CaF_2	Al_2O_3 (0.06)	10 m.o	773	< 10^2 (Fujitsu <i>et al</i> 1985)

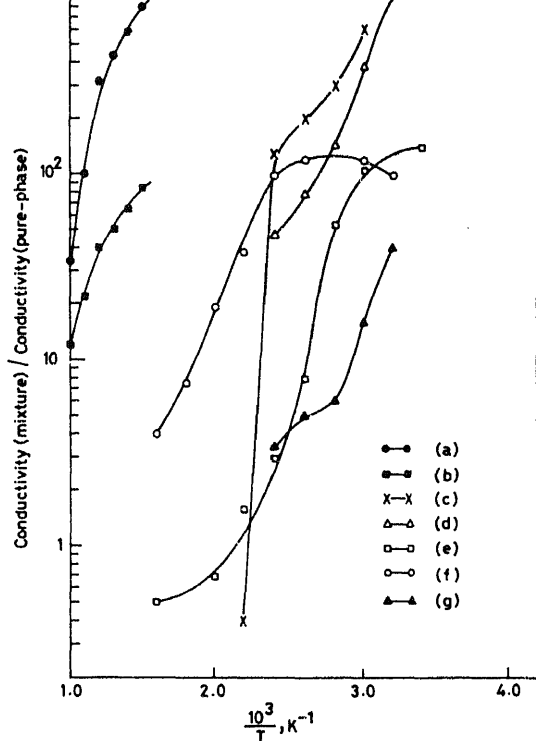


Figure 1. Enhancements in ionic conductivities for various mixtures as a function of temperature: (a) $\text{CaF}_2\text{-CeO}_2$ (2 m/o, $0.01 \mu\text{m}$), (b) $\text{CaF}_2\text{-Al}_2\text{O}_3$ (2 m/o, $0.02 \mu\text{m}$), (c) $\text{AgI-Al}_2\text{O}_3$ (30 m/o, $0.06 \mu\text{m}$), (d) AgI-AgBr (20 m/o), (e) $\text{AgCl-Al}_2\text{O}_3$ (3 v/o, $0.3 \mu\text{m}$), (f) $\text{CuCl-Al}_2\text{O}_3$ (10 m/o, $0.06 \mu\text{m}$), and (g) AgI-flyash (13.5 w/o) (m/o = mole %; v/o = volume %; w/o = weight %).

The factors which produce such an enhancement in ionic conductivity of these dispersed solid electrolytes are:

(a) **Temperature:** As is evident from figure 1, the relative enhancements in ionic conductivity of the dispersed solid electrolytes, with respect to their pure phases, are substantially higher at low temperatures. Also, a decrease in activation energies for ion migration with respect to pure phases have been observed as shown in table 2. The conductivities of the dispersed solid-electrolytes and those of the pure phases become almost the same at high temperatures in many systems like AgCl-SiO_2 (Maier 1985a), $\text{LiI-Al}_2\text{O}_3$ (Liang 1973) and $\text{CuCl-Al}_2\text{O}_3$ (Jow and Wagner 1979). However, for the systems $\text{CaF}_2\text{-Al}_2\text{O}_3$ and $\text{CaF}_2\text{-CeO}_2$ (Vaidehi *et al* 1986) there is a break in the conductivity of the dispersed phase. For all temperatures where measurements have been made, the conductivity of the dispersed electrolyte in these systems is higher than that of pure CaF_2 . Difference between the conductivities of the dispersed and pure phases has also been observed upto the melting point for the AgI-AgBr system (Shahi and Wagner 1982b), in which there is solid solubility of the dispersed phase in the matrix.

Table 2. Summary of electrical transport data.

Material/composition	Defect migration energies (eV)	Defect formation energies (eV)	
		Vacancy	Interstitial
AgI (pure) ^a	0.56	0.3	0.14
AgI + 30 m/o hydrated Al ₂ O ₃ ^a	0.26		
AgI + 10 m/o SiO ₂ ^a	0.29		
AgI + 13.5 w/o flyash ^a	0.26		
AgCl ^a	0.8	0.29	0.045
AgCl + 13 m/o Al ₂ O ₃ ^a	0.31		
AgCl + 11 v/o SiO ₂ ^a	0.30		
AgBr ^a	0.75 to 0.8	0.33	0.14
AgBr + 10 v/o Al ₂ O ₃ ^a	0.35		
CaF ₂ ^b	0.91	0.51	0.92
CaF ₂ + 2 m/o Al ₂ O ₃ ^b	0.71		
CaF ₂ + 2 m/o CeO ₂ ^b	0.66		
LiI ^a	0.8		
LiI + 40 m/o Al ₂ O ₃ ^a	0.42		

^a After Maier 1985b; ^b after Vaidehi *et al* 1986.

(b) *Concentration of the dispersoid*: The ionic conductivities of dispersed solid-electrolytes generally exhibit a maximum at a certain concentration (see figure 2). A broad break, covering a large range of concentrations, has also been observed in HgI₂-Al₂O₃ (Pack 1979; Pack *et al* 1980), and AgI-predried Al₂O₃ (Shahi and Wagner 1982a). It is noteworthy that unlike the case for solid electrolytes dispersed with hydrated alumina, the enhancements in the conductivities of solid electrolytes dispersed with predried alumina are insignificant. The role of hydroxyl ions in enhancing the ionic conductivities of the dispersed solid-electrolytes is hence not ruled out.

(c) *Particle size of the dispersoid*: The enhancement in ionic conductivities is a strong function of the particle size of the dispersoids. Figure 3 shows the variation of ionic conductivity with particle size for CuCl-10 mole % Al₂O₃ (Chang 1978) at 373 K. The conductivity decreases with increase in particle size. Similar behaviour has also been reported (Shahi and Wagner 1982a) for other systems also. As is evident from figure 3, the conductivity enhancements for a given concentration of the dispersoid are large for small particles. Probably, the large dispersoid particles block the path for ion conduction in these solid electrolytes.

(d) *Method of preparation*: A dispersed solid-electrolyte system is prepared by mixing the two components—ionic conductor and insulator—followed by sintering. When the particle size of the dispersed solid is much smaller than that of the host matrix, the dispersed solid-electrolytes prepared by the powder method would contain most of the dispersoids along the grain boundaries. The sintering temperature is found to influence the conductivity of dispersed solid electrolyte. Figure 4 illustrates the variation of conductivity with calcining temperature for CaF₂-Al₂O₃ (Fujitsu *et al* 1985) which exhibits a maximum at 1773 K. Jow and Wagner (1979) have reported similar results for

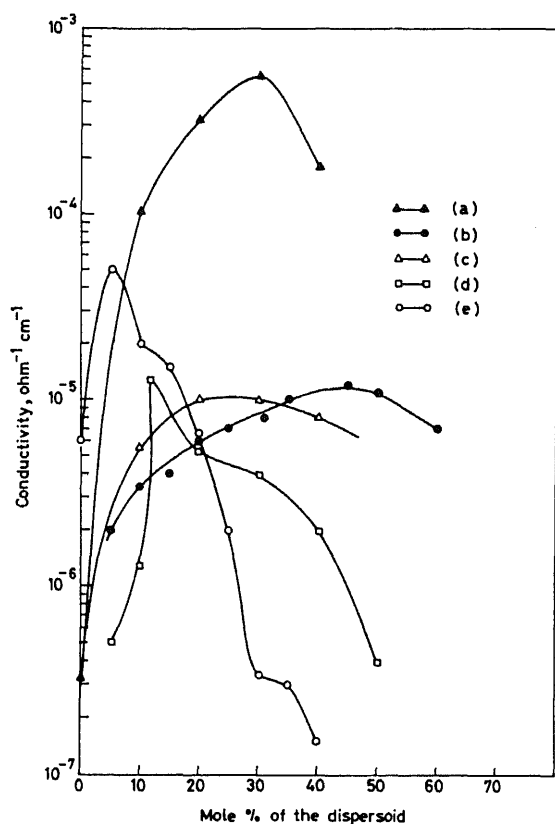


Figure 2. Variation of ionic conductivity with concentration of dispersoid for various dispersed solid-electrolytes: (a) AgI-hydrated Al_2O_3 (25°C , $0.06\ \mu\text{m}$), (b) $\text{LiI-Al}_2\text{O}_3$ ($25 \pm 2^\circ\text{C}$), (c) AgI-predried Al_2O_3 (25°C , $0.06\ \mu\text{m}$), (d) AgI-flyash (24°C), and (e) $\text{CaF}_2\text{-Al}_2\text{O}_3$ (500°C , $0.06\ \mu\text{m}$).

4. Mode of conduction

In order to explain the conductivity behaviour of biphasic mixtures of materials several theoretical models have been advanced in the literature (Rayleigh 1892; Lichtenecker 1924; Landauer 1952; Maxwell 1965; Wagner 1972; Crosbie 1977, 1978; Pack 1979; Jow and Wagner 1979; Stoneham *et al* 1979; Maier 1984, 1985a, b). A number of different shapes and arrangements of the mixture can be visualized. Conductivities of a bimetallic mixture frequently expressed in metallurgical literature (Landauer 1952) are

$$\rho_M = x_1 \rho_1 + x_2 \rho_2, \quad (1)$$

where ρ_M is the resistivity of the mixture; x_1 and x_2 are volume fraction of materials 1 and 2 respectively; ρ_1 and ρ_2 are their respective resistivities. This would be correct if the materials were arranged in alternate layers, perpendicular to the direction of current flow. In such a model, the current cannot avoid the regions of high resistances, as it will

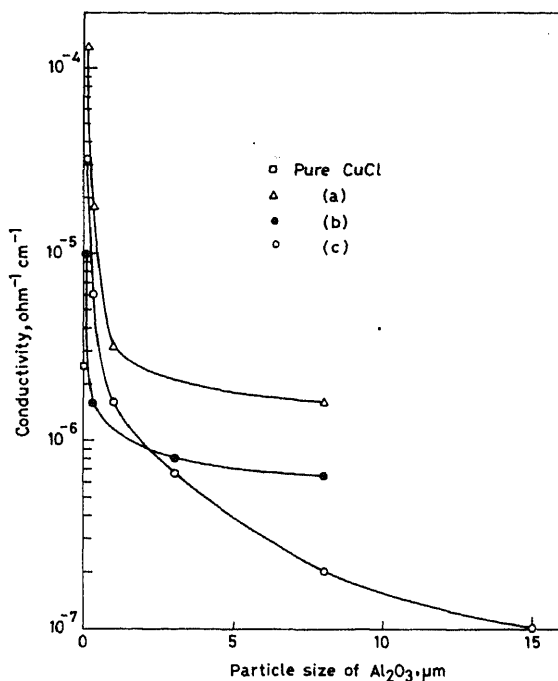


Figure 3. Variation of conductivity with the particle size of Al_2O_3 for various host matrices: (a) HgI_2 -25 m/o hydrated- Al_2O_3 (203°C), (b) AgI -30 m/o predried- Al_2O_3 (25°C), and (c) CuCl -10 m/o Al_2O_3 (100°C).

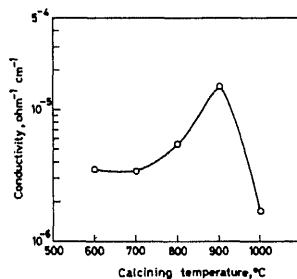


Figure 4. Effect of calcining temperature on conductivity for CaF_2 -20 m/o Al_2O_3 of $0.3 \mu\text{m}$ particle size.

two phases are passive. Therefore, (1) will give an upper limit for the resistivity. If the layers are parallel to the direction of current flow, then the total conductivity of the mixture, σ_M , will be given by

$$\sigma_M = x_1 \sigma_1 + x_2 \sigma_2. \quad (2)$$

Equation (2) will give an upper limit for the conductivity. The current can therefore flow straight through the regions of low resistivity preferentially, without having to

Another approximation, which agrees better with the measured values of the resistance of metallic mixtures was put forth by Lichtenecker (1924):

$$\rho_M = \rho_1^{x_1} \rho_2^{x_2}. \quad (3)$$

Equation (3) may be considered as an improvement over (1) as it incorporates the non-passive components of the two chemical phases to a certain extent. In comparing the results of existing theories with experimental results it becomes apparent that all methods of interpolating between σ_1 and σ_2 or between ρ_1 and ρ_2 give good results if the two conductivities are of the same order of magnitude. The validity of such theories can only be critically tested by considering the case where the conductivities σ_1 and σ_2 differ appreciably. It can easily be seen that (3) does not meet this requirement. If there is only a very small amount of material 2 with $\rho_2 = 0$, (3) gives $\rho_M = 0$. Actually, a few small particles of perfect conductor would not alter the conductivity of a medium appreciably, since most of the current's path would still be in a medium of finite conductivity. Similarly a small trace of 2 with $\rho_2 = \infty$ would give $\rho_M = \infty$ which is unreasonable.

Rayleigh (1892) treated the electrical conduction in biphasic systems by considering that material 2 exists in the form of spheres or cylinders, forming a rectangular array which is embedded in material 1 (figure 5). In this model, there exist lines of current flow which stay entirely within material 1 and are never interrupted by meeting an obstacle of material 2. On the other hand, current can never flow from a piece of material 2 to another piece of the same material without traversing a region of material 1. Therefore, even if there are equal volumes of 1 and 2, it will primarily be the conductivity of material 1 that predominates. Rayleigh's treatment is accurate only if the amount of material 2 is small compared to that of 1 or if the situation is one in which material 1 always envelops material 2. Physical arrangement in real systems rarely corresponds to the idealization in Rayleigh's model.

Wagner (1972) attempted to explain the conductivity behaviour of biphasic semiconductor-metal mixtures, such as Zn-metal dispersed in ZnO. Having found the existing theories to be inadequate, he introduced the concept of the existence of the space-charge region at the interface, caused by the charge density gradient (or potential gradient) due to the non-passive nature of the different components present in the mixture, at the interface. Following Wagner, Crosbie (1977, 1978) studied the electrical conduction in $\text{TiO}_2\text{-SiO}_2$ mixtures and explained the data using the equation:

$$\sigma(\text{dispersed solid})/\sigma(\text{host}) = \{1 + 0.83 g |Z| V_u \lambda / r_1^2\}. \quad (4)$$

Here, σ (dispersed solid) is the conductivity of the biphasic mixture, σ (host) is the

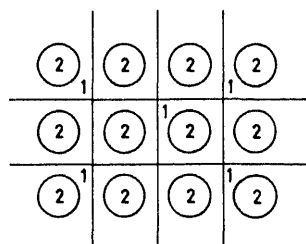


Figure 5. Rayleigh's model for two-phase systems.

conductivity of the pure host matrix; g is a structural factor 20; Z is the effective charge on the defects created; V_v is the volume fraction of dispersoid in the mixture; r_1 is the radius of the dispersoid particle and λ is the Debye length given by

$$\lambda = (8\pi e^2 c(\infty)/\epsilon kT)^{1/2}, \quad (5)$$

where ϵ is the dielectric constant of the medium at temperature T , k is the Boltzmann constant, $c(\infty)$ is the defect concentration in the bulk and e is the fundamental charge.

Jow and Wagner (1979) have extended this approach to explain the enhancement of ionic conductivity in $\text{CuCl-Al}_2\text{O}_3$. Akin to Wagner's approach, these authors also propose that ultrafine dispersoids (phase- A) form well defined space-charge regions in contact with the host electrolyte (phase- MX). Sphericity of the dispersoid particles assumed in the model (figure 6) gets support from the electron microscopy studies (Shahi and Wagner 1982a). An increase in defect concentration in this space-charge region enhances the ionic conductivities of the electrolyte. The total conductivity of the biphasic mixture including the contribution from the space-charge (sc) region σ_{sc} , and neglecting the conductivity of insulating phase- A , is given by

$$\sigma = \sigma_0 + \sigma_{sc} \quad (6)$$

σ_{sc} , the space-charge region contribution, is calculated between distances r_1 and r_2 as shown in figure 6(c). In the spherical polar coordinates σ_{sc} will amount to:

$$\sigma_{sc} = \frac{\sum_i e\mu_i \left\{ \int_{r_1}^{r_2} \int_0^{\pi/2} \int_0^{2\pi} [n_i(r) - n_i(\infty)] r^2 dr \sin \theta d\theta d\phi \right\}}{\int_{r_1}^{r_2} \int_0^{\pi/2} \int_0^{2\pi} r^2 dr \sin \theta d\theta d\phi}. \quad (7)$$

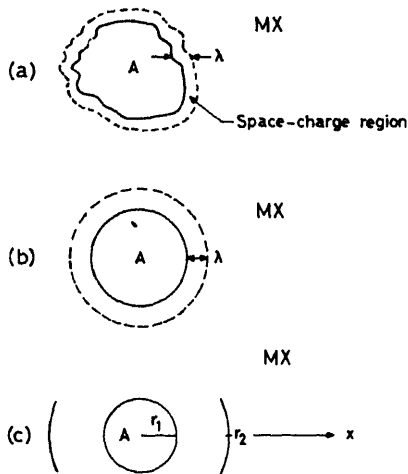


Figure 6. (a) Particle of A -phase embedded in MX -material and bearing a space-charge layer around it, (b) spherical approximation to the shape of A -phase particle, and (c) schematic cross sectional view of a single A phase particle of radius r_1 in the matrix MX .

$$\sigma = \sum_i n_i(\infty) e \mu_i + \sum_i e \mu_i \frac{\left\{ \int_{r_1}^{r_2} \int_0^{\pi/2} \int_0^{2\pi} [n_i(r) - n_i(\infty)] r^2 dr \sin \theta d\theta d\phi \right\}}{\int_{r_1}^{r_2} \int_0^{\pi/2} \int_0^{2\pi} r^2 dr \sin \theta d\theta d\phi} \quad (8)$$

Here, μ_i is the mobility of the i th defect species; $n_i(r)$ and $n_i(\infty)$ are the defect concentrations at a point r and in the bulk, respectively. The summation runs over all the different defect species. For $\lambda \ll r_1$, that is when the space-charge layer is much smaller than the size of the dispersoid particles the excess defect concentration in (8) is taken to be the arithmetic mean, $\langle \Delta n_i \rangle$, of the defect concentration at the surface and the bulk. Thus, σ_{SC} reduces to

$$\sigma_{SC} = \sum_i e \mu_i \langle \Delta n_i \rangle 4\pi r_1^2 \lambda / (4\pi/3)(r_2^3 - r_1^3). \quad (9)$$

Assuming that $(r_1/r_2)^3 = V_v$ the volume fraction of the dispersoid, (9) becomes

$$\sigma_{SC} = 3 \sum_i e \mu_i \langle \Delta n_i \rangle (\lambda/r_1) (V_v/1 - V_v). \quad (10)$$

Equation (10) gives only a qualitative indication of the temperature dependence of dispersed solid-electrolytes. The enhancements observed in ionic conductivities of dispersed-solid-electrolyte systems in relation to the pure host matrices are larger at low temperatures than those at high temperatures. This is envisaged by (10) since the Debye length, λ , decreases with increasing temperature. Equation (10) also explains the decrease in conductivity with increase in particle size of the dispersoid in conformity with the experimental findings (figure 3). This model is limited to small concentrations of the dispersoid and does not predict a maximum in conductivity of the dispersed solid-electrolyte at a particular concentration of the dispersoid as observed experimentally (figure 2). Besides, this model does not explain the mechanism leading to the enrichment of defect concentration in the space-charge regions of the various dispersed solid-electrolytes.

Recently, Maier (1984, 1985a, b) has proposed an approach for estimating the bulk conductivity of a dispersion of an insulator phase-A, in an ionically conducting matrix, phase-MX, employing the principle of parallel-switching (Maier 1985a). The physical situation adopted to estimate the total conductivity of the dispersed solid-electrolyte system is shown in figure 7. This model accounts for some of the inadequacies in the approach due to Jow and Wagner (1979). The model treats the space-charge region as a separate phase and considers each phase as a parallel resistor. The total conductivity, σ , of a dispersed solid-electrolyte given by

$$\sigma = \beta_A \phi_A \sigma_A + \beta_\infty \phi_\infty \sigma_\infty + \beta_{SC} \phi_{SC} \sigma_{SC}, \quad (11)$$

where, ∞ denotes the bulk MX; ϕ_i is the volume fraction of phase i ; β_i is a parameter describing the deviation from the ideal parallel-switching.

It would be appropriate to discuss the underlying defect chemistry of the dispersed solid-electrolytes to rationalize Maier's approach. Formation of Frenkel defects in a solid involves two steps (figure 8a). In the presence of the phase-A which does not react

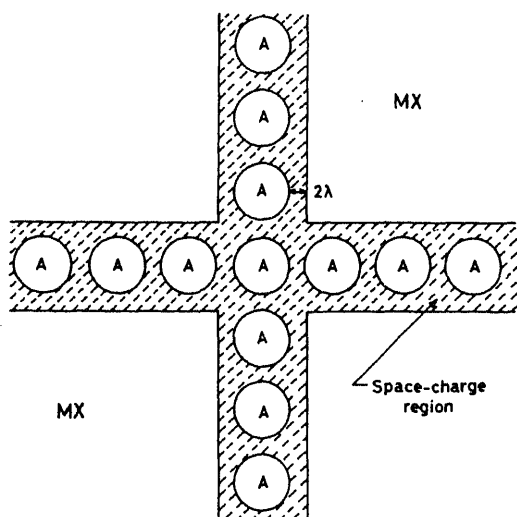
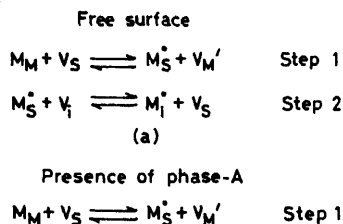


Figure 7. Coherent *A*-spheres forming crossing chains in the parallel-resistor model of Maier (1985a).

chemically with *MX*, the defect equilibrium may be affected. Attraction of metal ions (*M*) from the phase-*MX* by the chemical species present in phase *A* leads to enrichment of surface vacancies through step 2 of figure 8b. The process of attraction of the *M*-ions from the host electrolyte *MX* to phase-*A* proceeds in the manner shown in figure 9a. A repulsion of *M*-ions on the surface of *MX* by the chemical species on phase-*A* is equally feasible as shown in figure 9b. This would also lead to enrichment of surface vacancies as the forward reaction in step 2 of figure 8a will be more favoured. These attraction and repulsion processes are discrete and only one of them occurs for a given system under specific conditions. It was indicated earlier in our discussion that hydrated- Al_2O_3 dispersoid leads to a larger enhancement in conductivities than the predried Al_2O_3 (figure 2). This could be due to attraction of Ag^+ ions by the hydroxyl groups present in hydrated Al_2O_3 . In Schottky solids, however, a different situation exists. The



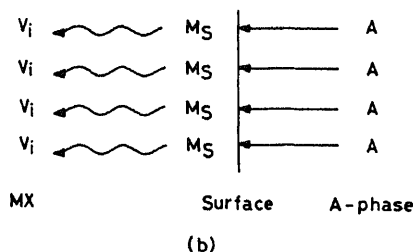
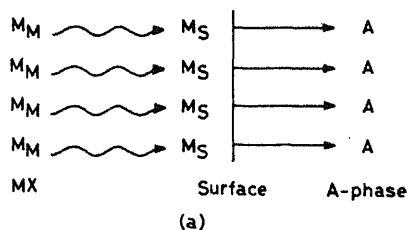


Figure 9. (a) Attraction mechanism by phase-A, and (b) Repulsion mechanism by A-phase.

defect equilibrium for formation of Schottky pairs is given in figure 10. In the presence of phase-A both cations and anions will compete for attraction and repulsion. Consequently, these two processes will be non-discrete in nature. It thus becomes difficult to predict categorically whether the conductivity of a solid with Schottky defects will be enhanced by a dispersed solid. On the basis of the above discussion, it becomes quite evident that the presence of the dispersoid phase-A in a Frenkel solid would always lead to enrichment of surface vacancies in the space-charge region but not necessarily so in a Schottky solid.

The electrical conductivity component due to the space-charge region obtained by Maier by the exact integration of (8) in one-dimension cartesian co-ordinates using an exponential variation of the defect concentration is

$$\sigma_{SC} = e(2\lambda)\mu_v(C_{v0}C_{v\infty})^{1/2}. \quad (12)$$

Here, μ_v is the mobility of vacancies; C_{v0} and $C_{v\infty}$ are the concentrations of vacancies at the surface and the bulk, respectively; 2λ , the length factor is assumed to be the thickness of the space-charge layer. The dispersoid particles are assumed to be spherical and surrounded by a spherical space-charge region of thickness 2λ . The volume of the space-charge region is obtained by subtracting the volume of inner sphere from that of

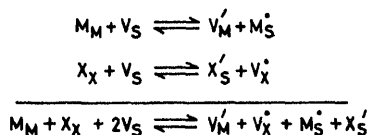


Figure 10. Formation of cation and anion vacancy pairs in Schottky solids.

the outer sphere and is given by

$$\sigma_{SC} = 3 \times (2\lambda/r_A)\phi_A \quad (13)$$

where r_A is the radius of the dispersoid particles. The total conductivity from (11) is thus given by

$$\sigma = (1 - \phi_A)\sigma_\infty + 3e\beta_{SC}2\lambda(\phi_A/r_A)\mu_v(C_{v0}C_{v\infty})^{1/2}. \quad (14)$$

Here, the conductivity due to the insulating phase-A has been neglected.

Equation (14) has been found to fit the experimental data of various dispersed solid-electrolytes fairly well, by adjusting the degree of non-ideal parallel-switching parameter, β_{SC} . Figure 11 shows the fit for $\text{CaF}_2\text{-CeO}_2$ and $\text{CaF}_2\text{-Al}_2\text{O}_3$ systems (Vaidehi *et al* 1986). Similar quantitative fits have been obtained for $\text{AgCl-Al}_2\text{O}_3$ and AgCl-SiO_2 (Maier 1985a) as well. The larger conductivity enhancements at low temperatures as compared to high temperatures are brought out correctly by (14). It is also obvious from (14) that as the particle size (r_A) of the dispersoid increases, the conductivity decreases as observed experimentally. The attractive feature of Maier's model is that it highlights the mechanism responsible for enrichment of surface

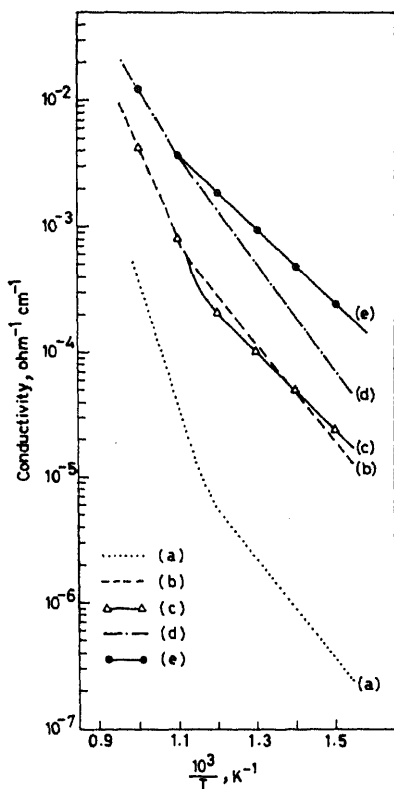


Figure 11. Variation of conductivity with temperature for: (a) pure CaF_2 , (b) calculated values for $\text{CaF}_2\text{-2 m/o Al}_2\text{O}_3$, (c) experimental values for $\text{CaF}_2\text{-2 m/o Al}_2\text{O}_3$ (d) calculated values for $\text{CaF}_2\text{-2 m/o CeO}_2$, and (e) observed values for $\text{CaF}_2\text{-2 m/o CeO}_2$.

vacancies in the space-charge region. Although this model is more quantitative than that due to Jow and Wagner, it has the same limitations.

Ionic conduction in dispersed solid-electrolytes has also been explained by Stoneham *et al* (1979). This model is an extension of Landauer's model (Landauer 1952) for the conductivity of a random mixture of two media in good electrical contact and with differing conductivities (figure 12). If the two media are labelled 1 and 2, one considers in turn the polarization of a sphere of each in an average medium. The average medium itself is taken to have consistently chosen conductivity appropriate to the aggregate of the two components. In dispersed solid electrolytes the situation is different. The model of Stoneham *et al* clearly denotes that the host electrolyte particles far from any particle of the insulating dispersoid should constitute one of the media and also that the model of the other component should recognize that the highly conducting boundary layer lies on a non-conducting core. The model also considers a structured sphere for calculating the polarization of the dispersoid particle including the boundary layer. It accounts for the concentration of the dispersoid in the host electrolyte. The spatial distribution of the conductivity, σ , near the dispersoid particle of radius, R , in a host matrix due to Stoneham *et al* (1979) is shown in figure 13a. According to Landauer's model, the conductivity of the system will not go to zero at any stage as there is no insulating phase present in biphasic metal mixtures. As has been indicated already, Landauer's approach is inadequate for application to dispersed solid-electrolyte systems due to a basic difference in the nature of the system itself. Taking the thickness of the space-charge region to be t , Stoneham *et al* found the conductivity of a dispersed-solid-electrolyte to vary as shown in figure 13b near the insulating dispersoid particle. Stoneham *et al* also suggested that it would be appropriate to envisage a screening-layer model in these systems and in such a situation the conductivity will vary continuously as shown in figure 13c, which is more realistic.

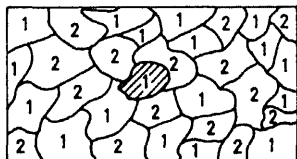
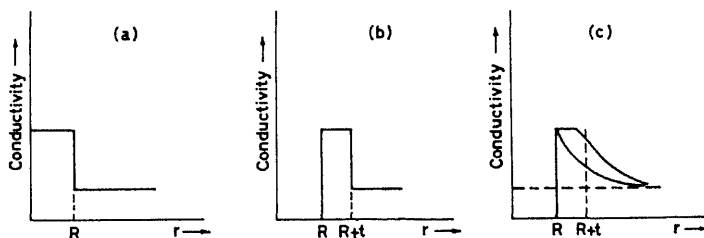


Figure 12. Landauer's polarization model.



Although, the model due to Stoneham *et al* successfully predicts that at high concentrations of the dispersoid a saturation in conductivity of the solid electrolyte should be observed, it does not account for the influence of temperature on the conductivity behaviour of the system.

5. Conclusions

No single theory successfully explains all the characteristic features of the dispersed-solid-electrolyte systems. It seems imperative to explore a model which could account for all the features of these dispersed solid-electrolytes. Such a model might provide a tool for tailoring newer and probably better solid ionic conductors. Experimental studies for estimating the conductivity contribution from the space-charge region would be most desirable. Calorimetric measurements (Khandhar *et al* 1984) have shown that the space-charge region is associated with a large excess enthalpy in the AgI-AgBr system. Measurement of the frequency dispersion of impedance in dispersed solid-electrolytes may be useful in estimating the conductivities of the space-charge region.

Acknowledgements

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Electrical transport in two-phase mixtures

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Abstract. There is considerable interest in the electrical transport in two-phase systems because of their possible technological applications. This paper describes the recent data obtained on the effect of different types of dispersoids on two types of matrixes, viz., NiO, a predominantly *p*-type semiconductor and AgI, a predominantly ionic conductor. It has been shown that the total electrical conductivities of these composites depend strongly on the nature of the dispersoid as well as the matrix. In both the cases, however, an interfacial region has been shown to play a significant role.

Keywords. Electrical conduction; two-phase mixtures; excess enthalpy; interfacial effect.

1. Introduction

The traditional approach of calculating the electrical conductivity of two-phase mixtures by taking the weighted average of the bulk conductivity of each phase does not take into account the changes in the charged particles due to the presence of an electrical double layer at the interface between these phases. Wagner (1972) first considered this possibility and postulated that the total electrical conductivity can be markedly affected because of the presence of the interfacial double layer. Subsequent investigations substantiated the deviation from the classical approach in a large number of systems, some of which have found interesting commercial applications. Liang (1973) reported that by the dispersion of Al_2O_3 in LiI the ionic conductivity increased by orders of magnitude. This composite was thus found to be suitable for high current density solid state batteries. In seemingly unrelated experiments Wright *et al* (1975) reported that the presence of Al_2O_3 in the chromia scales found on nickel-chromium alloys markedly reduce the oxidation rates of the alloy.

In spite of these scattered observations and their possible interesting applications, there do not appear to be systematic investigations and satisfactory explanations of the observed behaviour. The present paper summarises the latest contributions on this topic with possible explanations.

Depending upon their conductivity, solids are classified as metals, semiconductors and insulators. Semiconductors are further classified as *n*-type, *p*-type and ionic conductors. Various combinations of dispersoids and matrixes are possible. The examples of dispersion in two typical matrixes are described below, viz.,

- (i) dispersion in a semiconducting nickel oxide matrix;
- (ii) dispersion in predominantly ionically conducting AgI matrix.

2. Dispersion in a semiconducting NiO matrix

2.1 Ni_3S_2 in NiO

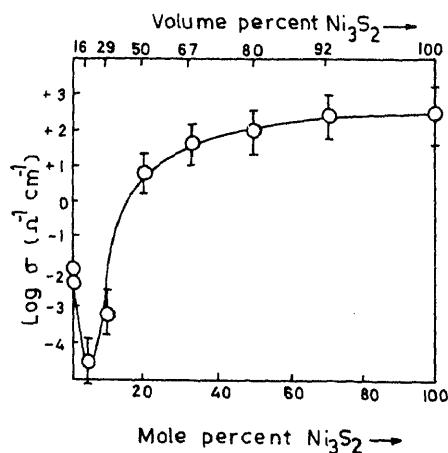


Figure 1. Electrical conductivity as a function of the composition of NiO-Ni₃S₂ mixtures at 600°C.

Specific conductivity as a function of Ni₃S₂ concentration is shown in figure 1 at 600°C. For samples of NiO heated in sulphur vapour for several days the conductivity is found to decrease only slightly and is also shown in this figure. Significant decrease in conductivity is observed for samples containing 5 mol % Ni₃S₂. Above this concentration conductivity again increases with increase in concentration of Ni₃S₂ upto 20 mol % Ni₃S₂ above which the variation in conductivity with increase in concentration of Ni₃S₂ is small. Below 20% Ni₃S₂ in NiO the composites behave like a semiconductor with predominantly *n*-type conductivity above 5% Ni₃S₂ and *p*-type below 5% Ni₃S₂ in NiO.

The activation energy for conduction estimated from the temperature dependence of conductivity is found to increase with increase in concentration of Ni₃S₂, attain a maximum at 5 mol % Ni₃S₂ and then decrease again with the increase in concentration of Ni₃S₂.

Microscopic examination of the composites showed that particle size of Ni₃S₂ varies from 10 to 100 μm while that of NiO is approximately 5 μm. Above 20 mol % Ni₃S₂ the interconnecting network of Ni₃S₂ is clearly observed (Tare and Wagner 1983a).

2.2 Ni in NiO

Nickel oxide in equilibrium with Ni is nearly a stoichiometric compound with very small number of point defects (Tretyakov and Rapp 1969). The electrical conductivity of samples containing varying concentrations of Ni is shown in figure 2 at 727°C. Mixtures containing more than 20 mol % nickel exhibit very high metallic type conductivity. Mixture containing less than 20 mol % Ni, however, behave like semiconductors. The addition of 1 mol % Ni decreases the conductivity. However, on increasing the concentration of Ni above about 1%, the conductivity also increases (Tare and Wagner 1983b).

The activation energy for conduction for all Ni-NiO samples, however, remained the same as that for pure NiO at 35 ± 2 k cal. The changeover from predominantly *p*-type

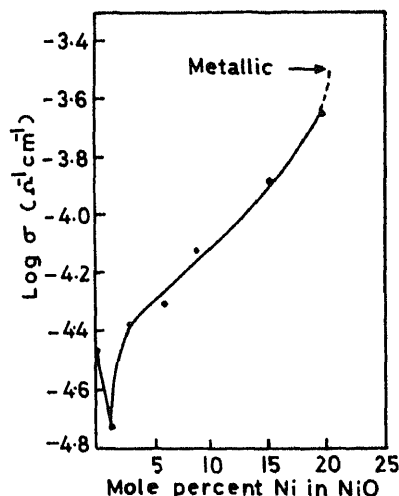


Figure 2. Electrical conductivity as a function of the composition of Ni-NiO mixtures at 727°C.

conductivity in NiO occurs to *n*-type at concentrations above about 1 mol % Ni. The particle size of both Ni and NiO was 5 μm.

2.3 CeO₂ in NiO

Cerium oxide, although reported to be a predominantly ionic conductor, exhibits *n*-type conductivity under certain conditions (Tuller and Nowick 1979). NiO is a *p*-type semiconductor. CeO₂ and NiO have negligible mutual solid solubility. Figure 3 shows the total conductivity of a NiO-CeO₂ two-phase system throughout the range of composition at 800°C. It can be seen that there is a small minimum in the conductivity curve at the CeO₂ rich end. For compositions ranging from 20 to 60 mol % NiO, the conductivity varies linearly with the composition. However, on either side of these limits the change is small. Similar behaviour was also noted in the variation of activation energy of conduction with composition in the temperature range 600 to 1000°C. It was difficult to determine the type of current carriers because of the low conductivity particularly for CeO₂ rich compositions. NiO rich compositions showed only *p*-type conductivity (Tare *et al* 1985b).

From the data reported above it is clear that when an electron donor phase is added to NiO, a *p*-type semiconductor, there is initially a decrease in conductivity. Further increase in the concentration of the electron donor phase results in conduction entirely due to the dispersoid. A minimum in conductivity at a fixed composition is thus observed in all the above cases. The concentration at which the maximum is observed is, however, dependent on the nature of the dispersoid and is found to increase with the decrease in electron concentration available for conduction in the dispersoid.

The initial decrease in conductivity is considered to be due to the trapping of holes at the interfaces due to the space charge layer. The number of mobile holes available for conduction thus decreases, resulting in a decrease in total conductivity. After all the

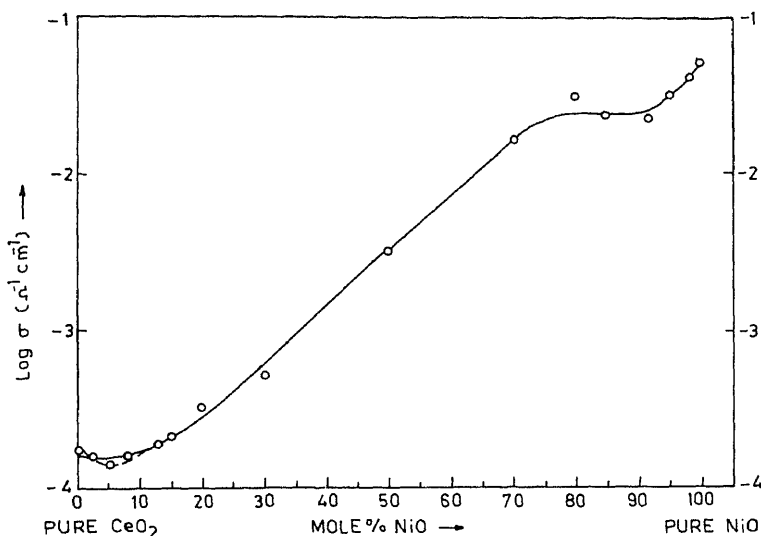


Figure 3. Electrical conductivity as a function of the composition of CeO_2 -NiO mixtures at 800°C .

available holes are thus trapped, further conduction is only due to the mobile electrons drawn from the dispersoid. The larger the number of electrons available from the dispersoid, the smaller the concentration required to trap all the available holes from the matrix.

The role of electrons from the dispersoid phase contributing to the total conduction has been discussed by Wagner (1972), who postulated that the inclusion of metal or metallically conducting particles provide clouds of excess electrons surrounding the individual inclusions as space charge layers. Accordingly the expression for the number of electrons in the medium between two metallic particles with radius r_1 and at distance $2r_2$ between the dispersoid particles is given by

$$n_2 = (1.1g \cdot f^{1/3} \epsilon kT) / (4\pi r_2^2 e^2)$$

where f is the volume fraction of the dispersoid, ϵ the dielectric constant, g depends upon the ratio of number of electrons at the surface of the dispersoid to the number in the matrix and is ≈ 20 . If the concentration of electrons available for conduction in the matrix is too small the overall conductivity is determined by the electrons from the dispersoid. Thus

$$\sigma = (22\epsilon kTu / 4\pi e) \cdot (f/r_1^2)$$

Therefore at constant temperature and for constant values of r_1 when $r_1 \ll r_2$, the conductivity is directly proportional to the volume fraction of dispersoid.

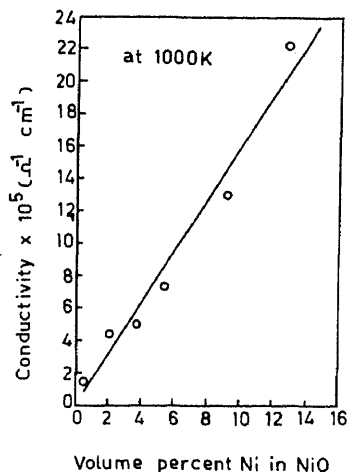


Figure 4. Electrical conductivity as a function of the volume fraction of nickel in NiO at 727°C.

3. Dispersion in predominantly ionically conducting AgI matrix

3.1 Al_2O_3 in AgI

Aluminium oxide, Al_2O_3 is an insulator. The effect of the dispersion of several types of insulating particles on the conductivity of AgI-insulator composites has been investigated by Shahi and Wagner (1981). All types of insulating particles were found to increase the conductivity whereas according to the conventional approach the conductivity is expected to decrease. The effect of insulating particles of Al_2O_3 as the dispersoid in an AgI matrix have been investigated in greater detail. Figure 5 shows the change in conductivity of the AgI- Al_2O_3 composite as a function of temperature and concentrations of Al_2O_3 in the temperature range 25 to 200°C. Figure 6 shows the change in conductivity as a function of concentration of Al_2O_3 at 25°C for β AgI and at 200°C for α AgI. Whereas the conductivity is found to decrease with increase in concentration of Al_2O_3 in α AgI, considerable enhancement in conduction is observed in β AgI. Another interesting observation is the occurrence of pseudo-hysteresis for the $\beta \rightarrow \alpha$ transformation. A typical feature of this hysteresis is that while the transformation temperature during the increasing temperature cycle i.e. for $\beta \rightarrow \alpha$, remains fairly same, the temperature of $\alpha \rightarrow \beta$ transformation during cooling deviates from true transformation temperature. Figure 7 shows that the deviation ΔT varies linearly with the increase in the concentration of the dispersoid. The enhancement of conductivity and the extent of hysteresis depend only on the surface area (figure 8). Thus for larger particle size, the concentration of the dispersoid needed to achieve the same effect is also higher (Chowdhury *et al* 1985).

3.2 AgBr in AgI

Silver bromide and silver iodide are both predominantly ionic conductors. The solubility of AgBr in AgI is about 10–15 mol% while that of AgI in AgBr is

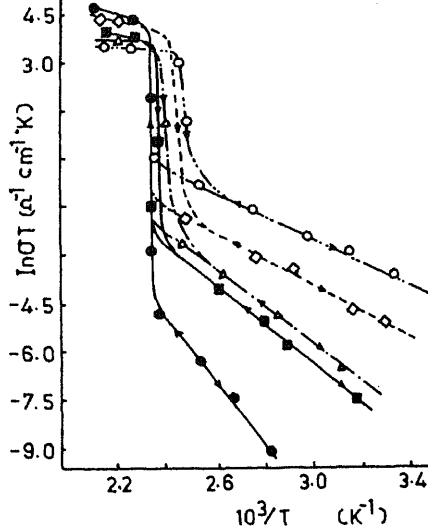


Figure 5. Electrical conductivity as a function of the temperature at various concentrations of Al_2O_3 in AgI [closed circles—AgI; closed squares—AgI + 10 mol % Al_2O_3 (0.3 μm); open triangles—AgI + 20 mol % Al_2O_3 (0.3 μm); open squares—AgI + 10 mol % Al_2O_3 (0.06 μm); open circles—AgI + 20 mol % Al_2O_3 (0.06 μm)].

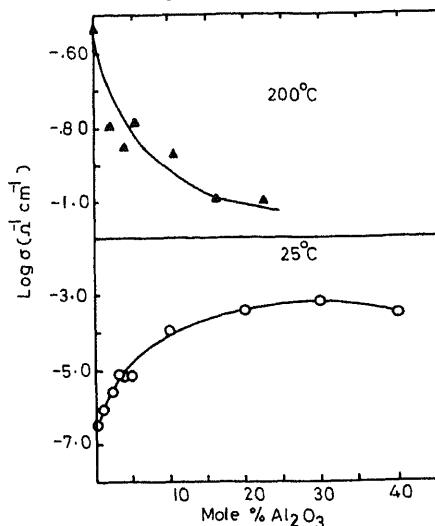


Figure 6. Electrical conductivity as a function of the mole and volume percent of Al_2O_3 (0.06 μm).

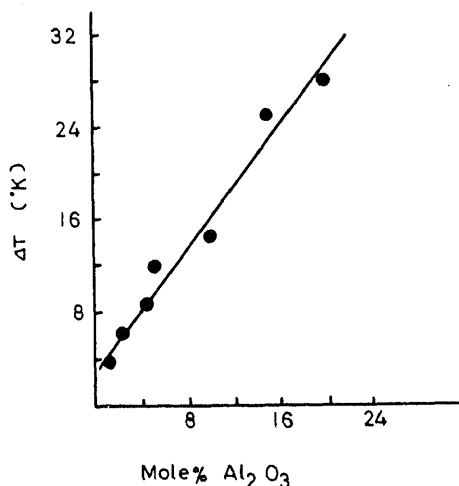


Figure 7. ΔT as a function of the mole % Al_2O_3 (0.06 μm).

approximately 30 mol % at 25°C (Shahi and Wagner 1981). For compositions between these solubility limits there is a two-phase region. The conductivity throughout the range of AgI-AgBr composition has been investigated by Shahi and Wagner (1981) and is shown in figure 9. It is clear that, instead of having a linear variation of conductivity in the two-phase region, a maximum in conductivity is observed at around 25 mol %

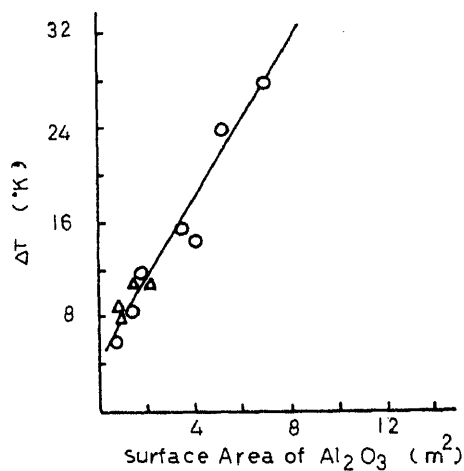


Figure 8. ΔT as a function of the surface area of Al_2O_3 per gram of AgI [circles— Al_2O_3 ($0.06 \mu\text{m}$); triangles— Al_2O_3 ($0.3 \mu\text{m}$)].

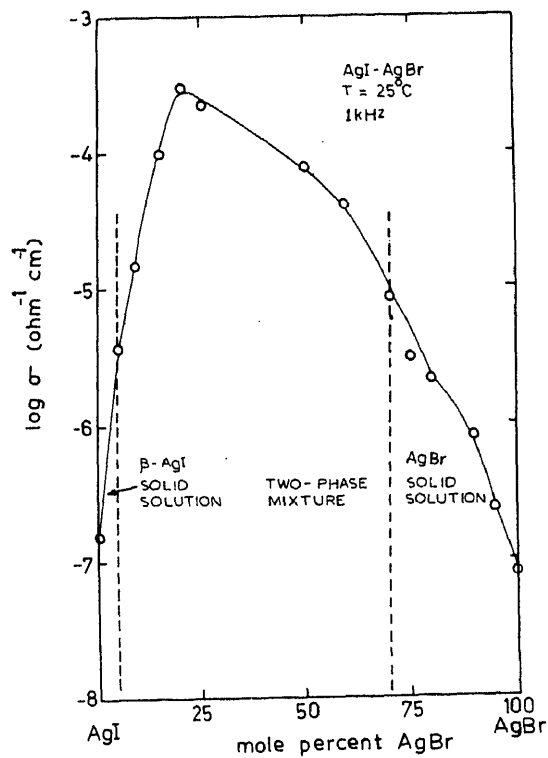


Figure 9. Electrical conduction as a function of the composition of AgI-AgBr mixtures at 25°C .

AgBr in AgI. Both AgI and AgBr are predominantly ionic conductors having Frenkel disorder. The conductivity is essentially due to the migration of silver ion interstitials or silver ion vacancies. The enhancement in conduction indicates the creation of additional defects. The experimental evidence for the generation of additional defects has been recently obtained by precise calorimetric measurements (Khandkar *et al* 1984). It has been shown that there is a finite difference in enthalpy content (excess enthalpy) between the molten and the mechanically mixed two-phase mixtures of the two end compositions in the AgI-AgBr system. Figure 10 shows that this enthalpy difference is maximum at equimolar end compositions. The densities of the end compositions are not very different. Hence, this composition is also the composition of maximum interfacial area.

Occurrence of maxima in excess enthalpy at compositions which generate maximum surface area indicates that additional defects are created at the interface and that the excess enthalpy is due to the formation of these additional defects.

Pack (1979) postulated that the total conductivity in a two-phase mixture consists of three parts, viz., (i) that due to the matrix, (ii) that due to the interfacial layer, and (iii) that due to the dispersoid. Thus

$$\sigma_{\text{total}} = \sigma_1(1 - V_v) + G \cdot S \cdot (1 - V_v)^2 + \sigma_2 \cdot V_v,$$

where

σ_1 = conductivity of the matrix material;

σ_2 = conductivity of the dispersoid material;

V_v = volume fraction of the dispersoid;

S = surface area created by dispersoid per unit volume of the mixture;

G = factor accounting for the excess charges per unit volume of the mixture.

Thus, the excess conductivity is considered to be due to the presence of an interfacial layer.

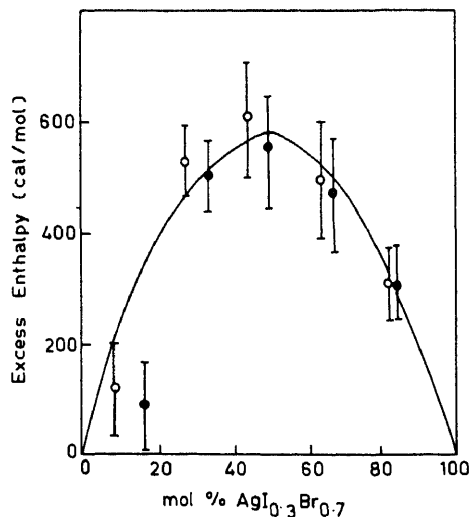


Figure 10. Excess enthalpy $(H_{518} - H_{298})_{\text{melted}} - (H_{518} - H_{298})_{\text{unmelted}}$ as a function of AgI-Br in AgI-Br (●) and AgI-Br (○).

The generation of defects at the interface is schematically shown in figure 11. If we assume λ as the Debye length, the maximum number of defects are created in this region. Thus a highly conducting region surrounds a dispersoid and hence the overall increase in conductivity is expected. Occurrence of maxima at different compositions for conductivity and excess enthalpy is probably due to the fact that whereas conductivity depends upon mobility as well as the number of migrating species, the excess enthalpy depends upon the number only (Khandkar *et al* 1984).

It is difficult to visualise the exact nature and type of the defects created at the interface. However, data obtained on $\text{AgI-Al}_2\text{O}_3$ composites suggests that the dispersion of Al_2O_3 in AgI is associated with additional cation vacancies at the $\text{AgI/Al}_2\text{O}_3$ interface for both α - and β - AgI . At high temperatures α - AgI has the so-called average structure in which all silver ions are moving in between relatively immobile iodine ions in a *bcc* arrangement. Silver ion mobility in this phase is so high that equilibrium between various defects is easily attained. Consequently, when Al_2O_3 is introduced into α - AgI , the cation vacancies generated at the interface act as sinks for some of the mobile silver ions and the conductivity decreases. Since a critical concentration of silver ion interstitials is needed for the $\alpha \rightarrow \beta$ transition, this transition is delayed.

At lower temperatures in which β - AgI is stable, the equilibrium between defects is not easily achieved. Thus in this case the total conductivity is due to the highly conducting interfacial layer because of the creation of a large number of vacancies in addition to the contribution from each of the two phases present. Since the transition temperature depends on the number of defects in the bulk AgI which is not altered, the transition temperature remains unaffected by the presence of Al_2O_3 as the dispersoid.

4. Conclusions

It is thus clear from the above discussion that the region at the interface between two different phases plays an important role in influencing the total conductivity of a two-phase system. The contribution of the interfacial region depends upon the nature of the

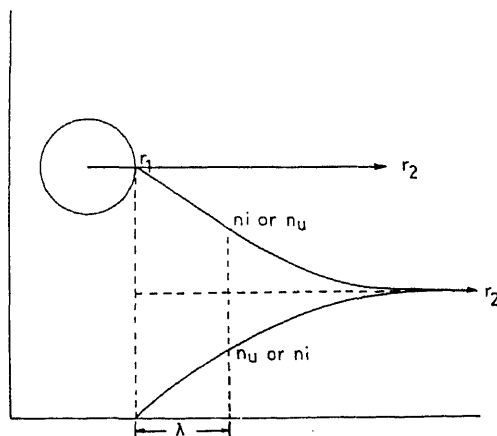


Figure 11. Schematic representation of the formation of defects at the interfacial region.

dispersoid as well the matrix. Much more systematic data is needed to formulate a generalised model.

Occurrence of two phases in a variety of situations is more the rule than the exception. For example, in corrosion of metals and alloys in mixed gaseous environment the corrosion product often consists of more than one phase. Since, in a situation when a compact mechanically perfect and adherent corrosion product is formed, the kinetics of corrosion strongly depends upon the transport properties of such a product layer, investigations of the type described in this paper become important. It may be possible to influence the rate of corrosion by monitoring the amount of the second phase in the corrosion product.

Besides this, considerable enhancement of conduction in ionic compounds, because of the presence of appropriate second phases, has an obvious potential for technological applications.

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Low temperature properties of glasses – unsolved problems

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Abstract. Glasses show very interesting behaviour well below the glass transition temperature. Inspite of various experimental observations, even simple quantitative explanations relating these relaxation phenomena to structural properties are absent. In this paper we have tried to point out a phenomenological approach to this problem by identifying certain parameters which we think can be used to characterize these relaxations.

Keywords. Glasses; relaxation; tunnelling model.

1. Introduction

Below the glass transition temperature glasses show very interesting behaviour. These have been studied by various experimental methods. However, till today a microscopic understanding of these low temperature properties has not been obtained. A reason for this may be the lack of any attempt for a structure-property correlation. It is true that most of these properties of glasses are universal and arise from its disorder structure. Nevertheless, the details for each material will be different. This is because most of this low temperature behaviour arises from low energy structural rearrangements occurring most probably in the scale of nearest or next nearest neighbour. Thus the details of these structural rearrangement should be strongly dominated by short range structural order. In this paper we identify what we think are the outstanding problems in glasses below T_g . Due to size limitations our discussions are not going to be extensive, where appropriate we will refer to existing references.

2. The problem of relaxation

Most of the observed properties in glasses below T_g have their origins in relaxation of some type. So the crucial issue here is the existence of particle motion in a localized scale and over a time scale which has a wide distribution. This particle motion is in addition to the already existing lattice vibrations which occur at a relatively faster rate. A good review of particle motion in glasses has been given by Rao and Parthasarathy (1985).

To show that relaxations in glasses never stop even at temperatures much lower than 1 K we refer to figure 1. This figure shows internal friction (Q^{-1}) in vitreous silica in a temperature range 0.01 K to 1000 K. At very high temperature, the rise in internal friction is due to glass transition (henceforth called α -relaxation) which is marked by large scale structural change. At low temperature the peak in Q^{-1} is generally called β relaxation. Below this peak Q^{-1} remains flat for a while and then decreases only at temperatures below 0.1 K. This behaviour is related to the existence of very low frequency excitations which we will refer to as two level system (TLS) relaxation (the

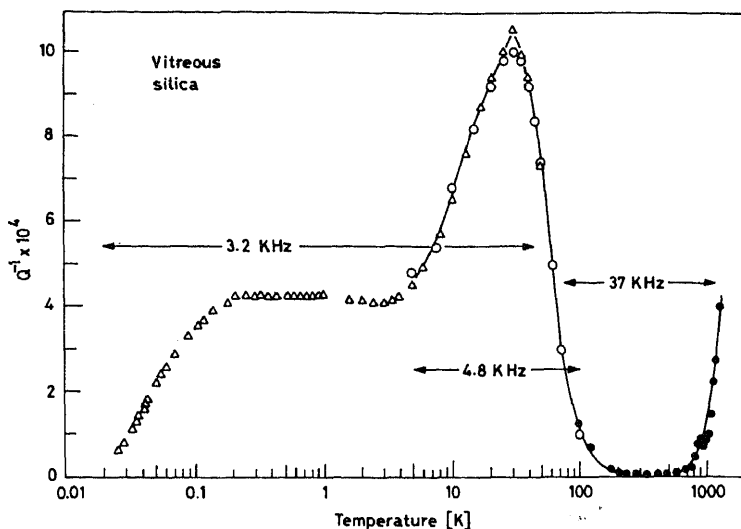


Figure 1. Internal friction (Q^{-1}) of vitreous silica from $T = 0.02$ K to $T = 1000$ K (Δ Raychaudhuri and Hunklinger 1984; $\circ$ Scott and MacGrone 1970; $\bullet$ Silvertsen 1953).

meaning of which will become apparent shortly). α , β and TLS relaxations signify three different types of relaxation mechanisms. While α relaxation involves structural changes (unlocking of liquid-like defects as T increases through T_g) involving higher energy, β relaxation involves localized structural changes. But both of them are classical thermally activated crossing of barriers although not of the pure Arrhenius type. TLS relaxation also involves localized structural changes, probably of the same type as in β relaxation but the mechanism of relaxation is quantum mechanical in origin.

These relaxation mechanisms may themselves be interrelated. But nothing can be said at this moment of what the interrelation is. The key problem in the physics of glass is relaxation and the key question is what is relaxing. The problem, as pointed out earlier, is one of structure property correlation. What we mean by structure-property correlation may be qualified as follows. First, it is necessary to identify the parameters which may be said to represent a quantitative measure of the relaxation process. Second, these parameters should be linked with some bulk properties of the glassy system. These bulk properties now need to be linked to actual structures through a structural model. It is from this model, we hope, that a microscopic understanding of these relaxation mechanisms will emerge. The task now is two-fold. First, it is necessary to identify on a semi-empirical basis the correlation of relaxation with structural parameters and second, to actually invent simple models which will explain the main aspects of these semi-empirical correlations. Unfortunately, such an approach is absent in this problem.

In the following, we will discuss briefly some important features of β and TLS relaxations and will try to point out what are the important relaxational parameters.

3. β -relaxation

The phenomenon of β relaxation is studied mainly by mechanical experiments (Hunklinger and Arnold 1976) or dielectric experiments (Johari 1976). In mechanical

experiments ultrasonic frequencies were generally used earlier. But measurements in insulating glasses at audio frequencies have also been done in the past. Recently β relaxation in metallic glasses has also been studied extensively by using audio-frequency techniques (Barmatz and Chen 1974; Raychaudhuri 1986).

In figure 2 we show ultrasonic attenuation in a number of glasses at low temperatures at a frequency of 20 MHz. In table 1, we list these materials, their glass transition temperatures (T_g) and the temperature T_m where the maximum occurs. It can be seen that T_m/T_g shows extremely wide variation from 0.03 (for SiO_2) to 0.27 (for GeS_2). Of these the case of polymethyl methyl acrylate (PMMA) and polyethyl methyl acrylate (PEMA) is particularly interesting. Substitution of a methyl group by the heavier ethyl group shifts T_m/T_g by a factor of 5. This shift is due most probably to the increase in activation energy of relaxation.

In ultrasonic or mechanical experiments it is difficult to obtain data over a large frequency range. Generally, the frequency here is kept fixed and the temperature is varied. In case of dielectric relaxation, however, it is easier to obtain data in the frequency domain. Studies of relaxation by the dielectric method in a number of glass forming systems have been made (Johari 1976). From all these studies it is obvious that the β relaxation peak has a large width. The first attempt to fit the experimental ultrasonic data was made by Hunklinger. He used a distribution of barrier heights $P(V)$

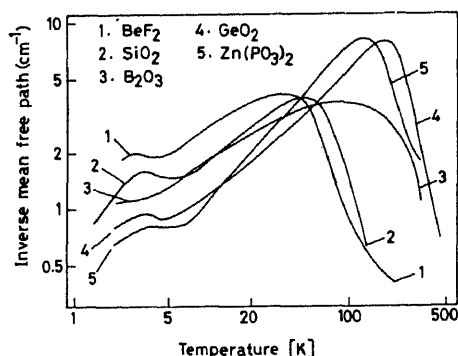


Figure 2. Ultrasonic attenuation in various glasses at low temperature at 20 MHz (Hunklinger and Arnold 1976).

Table 1. Ultrasonic β -relaxation peaks in glasses (at 20 MHz)

	Material							
	GeS_2	GeS_4	PMMA	PEMA	SiO_2	GeO_2	BeF_2	B_2O_3
T_g	750 K	625 K	374 K	338 K	1475 K	853 K	623 K	525 K
T_m	200 K	150 K	15 K	70 K	50 K	170 K	30 K	75 K
T_m/T_g	0.27	0.24	0.04	0.21	0.03	0.20	0.05	0.14

given as (Hunklinger and Arnold 1976)

$$P(V) = [P_0/V_0 \sqrt{2\pi}] \exp[-(V - V_m)^2/2V_0], \quad (1)$$

where $P_0 = \int_0^\infty P(V) dV$, $2V_0$ = width at half maximum and V_m is the centre. A similar expression has also been used (Berret *et al* 1985) to fit ultrasonic data on another glass (La SF7). However, the physical origins of these parameters are not clear. Recently Birge *et al* (1984) used an expression of the type given below to explain β relaxation in $(\text{KBr})_x (\text{KCN})_{1-x}$

$$P(V) = [1/(\pi\sigma)^{1/2}] \exp[-(V - V_m)^2/\sigma^2], \quad (2)$$

where σ is the temperature dependent width.

A recent theory of $(\text{KBr})_{0.5} (\text{KCN})_{0.5}$ explains the physical meaning of the parameters in (2). (Sethna *et al* 1984; Meissner *et al* 1985). We have investigated the available data of dielectric measurements of β -relaxation and found an expression of the type (2) can fit most of the data (Rajeev and Raychaudhuri 1986). We are now trying to correlate these fit parameters with physical quantities as a first step to make a model for β -relaxation.

4. TLS-relaxation

In 1971 it was observed that thermal properties of glasses are substantially different from their crystalline counter parts (Zeller and Pohl 1971). Below 1 K, the specific heat varies almost linearly with T whereas in crystals it show a Debye T^3 law (see figure 3). The thermal conductivity also shows a quadratic temperature dependence (see figure 4). This behaviour is now found to be universal to all glasses. We refer to two review articles for a detailed discussion (Phillips 1981; Hunklinger and Raychaudhuri 1986).

It is now generally believed that this excess specific heat and low thermal conductivity

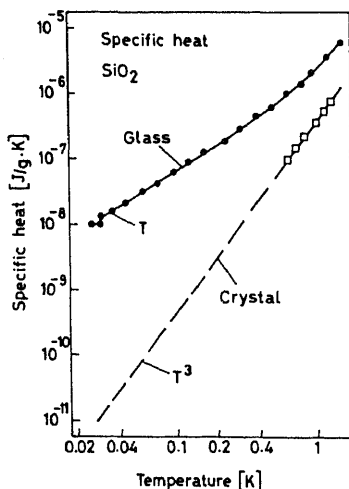


Figure 3. Specific heats of vitreous silica and crystalline quartz at low temperature (Zeller and Pohl 1971).

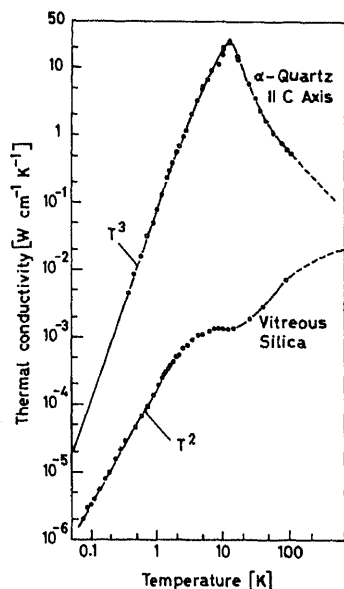


Figure 4. Thermal conductivities of vitreous silica and crystalline quartz (Zeller and Pohl 1971).

of glass is caused by excess excitations which are like two level systems (TLS). The TLS is believed to arise from tunnelling (quantum mechanical) of atoms or molecules (Anderson *et al* 1972; Phillips 1972). However, not much is known about the tunnelling units in actual glasses.

The low temperature acoustic and dielectric behaviour of glasses are mainly controlled by relaxation of these TLS. The TLS can also resonantly interact with lattice vibration (phonons) giving rise to the quadratic thermal conductivity. The references mentioned above discuss in detail all these aspects. In this paper we will point out what we think are the important parameters in TLS relaxation and the recent attempts to correlate them to bulk material properties. In the tunnelling model the two most important parameters are $\bar{P}$ the density of states of TLS and the deformation potentials for TLS—lattice interaction. At present these two have to be obtained from experiments (Hunklinger and Raychaudhuri 1985). The task is now first to obtain at least empirical correlation of $\bar{P}$ and γ with other properties like glass transition temperature (T_g), sound velocity etc. From this correlation a model of tunnelling units can then be made.

The first attempt in that direction has already started. The earliest correlation to be observed was between l (the phonon mean free path, which contains both $\bar{P}$ and γ) and T_g (Reynolds 1979). Later a correlation was found between $\bar{P}_0$ and T_g (Raychaudhuri and Pohl 1981, 1982; Doussineau *et al* 1983). Recent studies (MacDonald *et al* 1985) support the correlation of l and T_g . Recently these measurements have been extended to glass forming systems with lower T_g (Reichert *et al* 1985) and in 21 glasses it has been found that a relation of the following type holds.

relation holds have T_g lying between 135 K and 1500 K. It can be seen that for glasses with $kT_g \approx \Delta$, $\bar{P} \propto T_g^{-1}$. Equation (3) is indeed a remarkable one. And in our opinion will be the starting point for many a theory and model in future.

The correlation of γ with other properties are not yet very successful. But it seems that in samples with low T_g , $\gamma \propto T_g$.

Much work is required in this field before a proper structure property correlation can be attempted.

5. Conclusion

The above discussion is intended to highlight the problems of low energy relaxation in glasses. As it can be seen there is scope for much work in this field. In our opinion to gain an understanding the attempt should be directed towards a structure property-correlation. In this paper we have shown that the first stage of identifying the relevant relaxation parameters and establishing an empirical correlation with other bulk properties is already on its way. In the next stage, even a simple model to explain these properties in a particular glass will be a great step forward.

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Magnetic resonance lineshapes in powdered and amorphous systems

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Abstract. A survey is made of the theory and applications of EPR and NMR absorption lineshapes observed in powdered and amorphous materials. The 'spin Hamiltonian' and 'resonance condition' formalisms are reviewed, and EPR and NMR lineshapes are discussed which typify the singularity characteristics in powdered materials. In the amorphous or 'glassy' state, the measurable spin resonance parameters often have to be viewed as being 'randomly distributed' according to a probability density function. Several recent probability-theory based approaches to lineshape computation for modelling the amorphous state are discussed.

Keywords. EPR; NMR; lineshapes; powder; amorphous materials.

1. Introduction

Over the past several decades, amorphous solids have continued to be of tremendous interest to chemists, physicists and material scientists alike, and the question of 'how to recover the solid state physics without the periodic lattice' (Müller-Warmuth and Eckert 1982) has challenged theoreticians and experimentalists alike. Among magnetic resonance spectroscopists, the interpretation of a variety of resonance absorption 'patterns' of amorphous systems, as well as the extraction of magnetic interaction parameters therefrom, often pose a fascinating problem. This is because several of the important molecular tensor properties such as the electron paramagnetic resonance (EPR) g -factors, hyperfine (A) and zero-field (D) interactions, the nuclear quadrupole interaction (Q) etc., appear *distributed* and spectroscopic information has then to be recovered by modelling the paramagnetic system by means of detailed lineshape simulation procedures.

The purpose of this survey is to review briefly the 'spin Hamiltonian' formalism representing the various interaction parameters and then to show how resonance conditions based on these spin Hamiltonians lead to typical and characteristic singularities in the absorption lineshapes of powdered materials. The formalism will then be modified in a variety of ways for the analysis of the 'glassy' or amorphous state. Finally we shall consider, with representative examples, the concepts and interpretive guidelines that have been demonstrated in recent years for the analysis of EPR and NMR lineshapes in typical amorphous and glass structures.

2. The spin Hamiltonian and the resonance condition

In the laboratory, one customarily records the magnetic resonance spectrum of a solid sample as the first derivative of resonant absorption versus the applied magnetic field,

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of the paramagnetic spin vector (nuclear spin $\mathbf{I}$ in the case of NMR and electron spin $\mathbf{S}$ in the case of EPR) with the field vector, $\mathbf{H}$. The various parameters of the spin Hamiltonian are then related back to the chemical bonding of the environment by means of appropriate theories of molecular electronic structure.

The aforementioned spin Hamiltonian denoted in its most general form by $\mathcal{H}$, is phenomenologically set up such that it has a leading term representing the 'Zeeman' interaction between $\mathbf{H}$ and the $\mathbf{S}$ or $\mathbf{I}$ spin vector, followed by successively smaller 'perturbations' representing various tensorial couplings. In EPR, it takes the most general form

$$\mathcal{H}_{\text{EPR}} = \beta_e \mathbf{H} \cdot \vec{g} \cdot \mathbf{S} + \mathbf{I} \cdot \vec{A} \cdot \mathbf{S} + \mathbf{S} \cdot \vec{D} \cdot \mathbf{S} + \mathbf{I} \cdot \vec{Q} \cdot \mathbf{I} - \gamma \hbar \mathbf{I} \cdot \mathbf{H}, \quad (1)$$

where the leading (or zero-order) Zeeman term defines the molecular g -tensor. The second term is the electron spin-nuclear spin 'hyperfine' interaction (A), and the third term (operative in the case of several unpaired electron spins being present in the valence orbital of the paramagnetic centre, e.g., Mn^{2+}) is the 'fine structure' (or crystal field) interaction (D). The last two terms of (1) are the nuclear quadrupolar (Q) and the nuclear Zeeman interaction, respectively, and are usually very small members in the above 'hierarchy' of perturbations (Raghunathan 1981), and could become important in special instances as we shall exemplify later on. In (1), β_e is the fundamental 'electronic Bohr magneton' unit, and γ is another fundamental interaction constant called the nuclear magnetogyric ratio. $\vec{g}$, $\vec{A}$, $\vec{D}$ and $\vec{Q}$ are symmetric second-rank tensors representing the anisotropic nature of the respective couplings.

In an entirely analogous fashion, one may set up an appropriate NMR spin Hamiltonian. Foremost among the interactions contributing to resonance lineshapes are the internuclear magnetic dipole-dipole interactions and (for nuclei with $I > \frac{1}{2}$) the nuclear electric quadrupole interaction with the surrounding electric field gradient. In many cases, one or the other of these two interactions can be neglected, e.g., for protons and ^{19}F the quadrupolar interaction is zero, whereas for deuterons, ^{11}B , ^{14}N etc., the quadrupolar interaction dominates. On this basis the solids of interest in NMR spectroscopy are usually referred to as *dipolar* and *quadrupolar*. Having established this dichotomy, we shall here consider the quadrupolar (amorphous) solids only, since dipolar solid lineshapes have been reviewed in detail in several places (see, e.g., Raghunathan 1982).

We shall, accordingly, write the NMR spin Hamiltonian as

$$\begin{aligned} \mathcal{H}_{\text{NMR}} &= -\gamma \hbar \mathbf{I} \cdot \mathbf{H} + \mathbf{I} \cdot \vec{Q} \cdot \mathbf{I} \\ &= H_0 + H_Q. \end{aligned} \quad (2)$$

In the above, the second term written in terms of appropriate components of the nuclear spin becomes

$$H_Q = \frac{e^2 q Q}{4I(2I-1)\hbar} [3I_z^2 - I^2 + \eta(I_+^2 - I_-^2)],$$

where $e^2 q Q$ is the experimentally measurable 'quadrupolar coupling constant' parameter involving the electric quadrupole moment, eQ , of the nucleus, and a component q of the electric field gradient (EFG) tensor with principal axis components

q_{xx} , q_{yy} and q_{zz} ($= q$). η is called the 'asymmetry parameter', and is given by

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \text{ where } |q_{xx}| \leq |q_{yy}| \leq |q_{zz}|.$$

When $H_Q < H_0$, we could consider the former as a perturbing term which splits the magnetic resonance absorption line into $2I + 1$ components.

Relating the experimental spectra to (1) and (2) requires that the spin Hamiltonian be diagonalised to yield the 'resonance condition', H_m —an expression for the magnetic field at which resonance occurs as a function of the principal-axis values of the tensor quantities, the resonance frequency ν , and the magnetic quantum number m_S or m_I . Of course, $\mathbf{H}$, being a vector, is specified both by its magnitude and its orientation with respect to the principal axis coordinate systems of the interaction tensor. The orientation of $\mathbf{H}$ with respect to the tensor axes in (1) and (2) will be specified by the Euler angles θ and ϕ , as defined in figure 1. The EPR resonance condition for the $(m_S - 1) \rightarrow m_S$, $m_I = 0$ transitions, to first-order, is given by (Taylor *et al* 1975):

$$h\nu = g\beta_e H + (Am/g), \quad (3)$$

where

$$g = [g_1^2 \sin^2 \theta \sin^2 \phi + g_2^2 \sin^2 \theta \cos^2 \phi + g_3^2 \cos^2 \theta]^{1/2},$$

$$A = [A_1^2 g_1^2 \sin^2 \theta \sin^2 \phi + A_2^2 g_2^2 \sin^2 \theta \cos^2 \phi + A_3^2 g_3^2 \cos^2 \theta]^{1/2}. \quad (4)$$

The resonance conditions based on the NMR Hamiltonian (2) may be established in a manner analogous to the above by recognising that, now, θ and ϕ are the Euler angles relating the direction of the magnetic field $\mathbf{H}$ and the symmetry axes of the EFG tensor. When perturbation theory is considered only upto first order (Cohen and Reif 1957),

$$\nu_m^{(1)} = \frac{E_m^{(1)} - E_m^{(0)}}{\hbar} = \frac{1}{2} \nu_0 (m - \frac{1}{2}) (3 \cos^2 \theta - 1), \quad (5)$$

where ν_0 is the central resonance frequency of the nucleus in the absence of quadrupolar effects. We see from (5) that the first-order shift $\nu_m^{(1)}$ vanishes for $m = \frac{1}{2}$. For half-integral spins, the central transition $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ is therefore not shifted in first order by quadrupolar interaction. The frequencies of the other allowed lines are, however, shifted and satellite

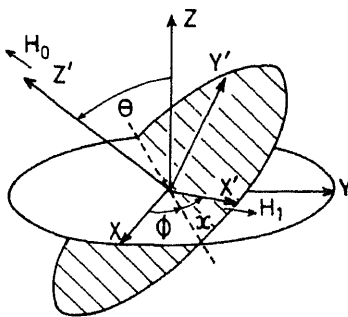


Figure 1. A general orientation of the magnetic field with respect to the molecular tensor

lines corresponding to transitions $m \leftrightarrow m - 1$ appear symmetrically on either side of the central line.

For the NMR of quadrupolar solids, therefore, perturbation theory considered upto second order is more revealing, and we obtain the second-order shifted resonance line, $\nu_m^{(2)}$, from the expression of $E_m^{(1)}$ which is an odd function of m (Jones *et al* 1963). In particular, when the EFG has axial symmetry ($\eta = 0$), the central $m_I = +\frac{1}{2} \leftrightarrow m_I = -\frac{1}{2}$ transition becomes shifted according to

$$\nu_{1/2}^{(2)} = (3/64) (1/\nu_0) (e^2 q Q)^2 (1 - 9 \cos^2 \theta) (1 - \cos^2 \theta). \quad (6)$$

3. Powder lineshapes and shape functions

In a finely crushed 'powder' specimen, spin sites occur with all possible orientations of their axes with respect to the direction of **H**. We consider these orientations as lying along the radii of a sphere, and partition the surface of the sphere into a grid determined by equal intervals of θ and ϕ . As can be readily seen, the surface area, and hence the solid angle, depends on the angle θ (see figure 2). In spherical polar coordinates, the differential element of solid angle $d\Omega = \sin \theta d\theta d\phi$. (This leads to the interesting result that there will be fewer spin sites within a given angular range near the parallel ($\theta = 0^\circ$) than within the same angular range near the perpendicular orientation ($\theta = 90^\circ$); therefore, for a near-axial system, the perpendicular features of the spectrum will be more intense than the 'parallel' ones.)

We can now, for any given transition, calculate a representative intensity for each area. Multiplying this intensity by the area and summing over all such areas should give, as the number of areas becomes large, the integrated intensity of the total powder 'lineshape'. Since, of course, the intensity of a transition varies with the value of the magnetic field which is being swept in the experiment, this process would have to be iterated for each chosen value of H to obtain the 'density of resonance

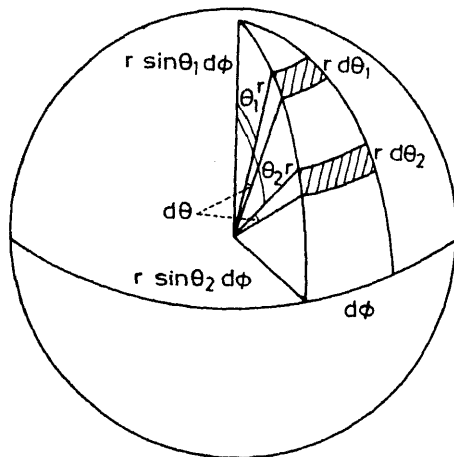


Figure 2. Dependence of the solid angle (area) on θ . Since the area changes as $\sin \theta$, the number of orientations in a given volume element arising from a grid determined by equal θ and equal ϕ intervals goes as $\sin \theta$.

fields'. Since we are interested only in relative intensities, we need to multiply the intensity of each area only by $\sin\theta$ if both θ as well as ϕ are stepped up in equal increments in our calculation. If we use equal increments of $\cos\theta$, we do *not* need any multiplier since $d(\cos\theta) = -\sin\theta d\theta$.

We thus make the important generalization that the magnetic 'resonance condition' for powders may be thought of as a surface in $(\cos\theta, \phi)$ space and can be written formally as $H_m = H_m(\cos\theta, \phi)$ with m denoting the appropriate transition, e.g., the $m_I \rightarrow (m_I - 1)$ NMR transition or the $(m_S - 1) \rightarrow m_S$ EPR transition. Accordingly in all numerical techniques of lineshape analysis (Maruani *et al* 1968; Taylor *et al* 1968; McDowell *et al* 1973; Jinguji *et al* 1976), the resonance condition is solved for all orientations given by a fine grid in $\cos\theta - \phi$ space. An equivalent, and often faster, computational procedure is to solve for the densities of resonance fields at a random distribution of points in $\cos\theta - \phi$ space generated by a Monte Carlo routine, and this is the procedure of choice in our laboratory.

By using either procedure, we see that the differential probability, $dP(H)$, of the resonance condition for a paramagnetic powder 'site' lying between H and $H + dH$ may be written in the normalised form (Jinguji *et al* 1976),

$$\begin{aligned} dP(H) &= d\Omega(\theta, \phi)/4\pi \\ &= d\cos\theta d\phi/4\pi, \end{aligned} \quad (7)$$

and the spectral lineshape at each resonance field obtained as

$$\frac{dP(H)}{dH} = (4\pi)^{-1} \frac{d\Omega}{dH} = (4\pi)^{-1} \left(\frac{dH}{d\Omega} \right)^{-1}. \quad (8)$$

The overall 'shape function' $S(H)$ which is of interest to us is therefore the weighted distribution of the resonance condition over all equally probable elements of $d\Omega$ integrated over all the allowed transitions. The lineshape information is stored in the inherent anisotropy of the spin site which is the same for all crystallites of the powder specimen. The Euler angles and the random orientations of the crystallites are the weighting factors which spread this information between the largest and smallest values in the 'distribution of resonance fields'. One writes $S(H)$ as

$$S(H) = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta (H_m) P_m(\theta, \phi), \quad (9)$$

where $P_m(\theta, \phi)$ is the transition probability for the m th component of the spectral absorption, being proportional to $S(S+1) - m_S(m_S-1)$ in the case of EPR and $I(I+1) - m_I(m_I-1)$ in the case of NMR. The $P_m(\theta, \phi)$ factor is usually independent of the solid angle and may therefore be taken outside the integral, although special cases of angular dependence of $P_m(\theta, \phi)$ have been discussed in the literature from time to time (Bleaney 1960; Isomoto *et al* 1970).

It is seen from (8) that lineshape singularities arise automatically at field values corresponding to critical points (Kottis and Lefebvre 1964; Maruani *et al* 1968; Coope 1969) of the function $H_m = H(\cos\theta, \phi)$, i.e., points where

$$\left(\frac{\partial H}{\partial \cos\theta} \right)_{x,y} = \left(\frac{\partial H}{\partial \phi} \right)_{x,y} = 0,$$

x and y being the coordinates of the critical point. A saddle point in the $H(\cos\theta, \phi)$ surface at location (x, y) indicates the presence of a *divergence* in the powder pattern at the field $H = H(x, y)$, whereas a relative extremum will give rise to a *shoulder* or *step* at $H(x, y)$. However, dipolar interaction mechanisms between neighbouring groups of spins somewhat broaden and smear out these singularities and therefore, in most actual cases, smoothed out shoulders and divergences are seen in the powder pattern at fields corresponding to H being aligned along one of the principal axes of the interaction tensor. For diagnostic purposes it is often sufficient to determine the locations of these principal features in the first and second derivative powder patterns (Weil and Hecht 1963; Lee 1981; Lee *et al* 1985).

On the other hand, to enable the *entire* theoretical 'step-shoulder-divergence' lineshapes to fit the experimental spectra, the ensemble of line positions calculated according to (9) is often convoluted with a suitable broadening function appropriate to the type of amorphous solid under study. For example, for the most often used Gaussian-shaped line of full width at half height w which characterises the small dipolar broadening mechanisms in most solids, the broadening function may be written as

$$f(H_m - H) \propto w^{-1} \exp[-4 \ln 2 ((H_m - H)/w)^2]. \quad (10)$$

A second source of line-broadening may be brought about by exchange interaction mechanisms in some solids (Bloch 1946; Van Vleck 1948), which may be approximated by the Lorentzian broadening function,

$$f(H_m - H) \propto w [(w^2/4) + (H_m - H)^2]^{-1}, \quad (11)$$

where w is the full width at half-height of the broadened line. In a general sense one may therefore consider the final, convoluted form of $S(H)$, (9), as

$$S(H) = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta f(H_m - H) P_m(\theta, \phi). \quad (12)$$

This is the standard lineshape function used whenever the powder sample may be thought of as a randomly oriented ensemble of *otherwise identical sites*. Although examples of these lineshapes abound in the literature, here we shall briefly typify the most frequently observed classes of EPR lineshape singularities as parts 'a' through 'h' of figure 3. In this figure, 'a' is the calculated lineshape for a paramagnetic site with an axial g -tensor and no hyperfine interaction (the simplest anisotropic case), and 'b' represents the field-derivative of the absorption in 'a'. The absorption lineshape for an axial g -tensor which is perturbed by an isotropic hyperfine interaction and its corresponding derivative shape are given in 'c' and 'd', respectively. In 'e', the typical EPR absorption for a site exhibiting an orthorhombic g -tensor is shown, while in 'f' its derivative shape is recorded. 'g' represents the absorption lineshape corresponding to an orthorhombic g -tensor as in 'e', but exhibiting further isotropic hyperfine interaction; the corresponding derivative lineshape is depicted in 'h'. In all these lineshapes, the g -values are determinable from the field positions indicated in the diagrams, using $g' = h\nu/\beta_e H$.

One simplifying assumption that has been implicitly made in the EPR resonance conditions, (1), (3) and (4), is that all tensor quantities have identical principal axes. This restriction can, of course, be removed by introducing additional adjustable trigono-

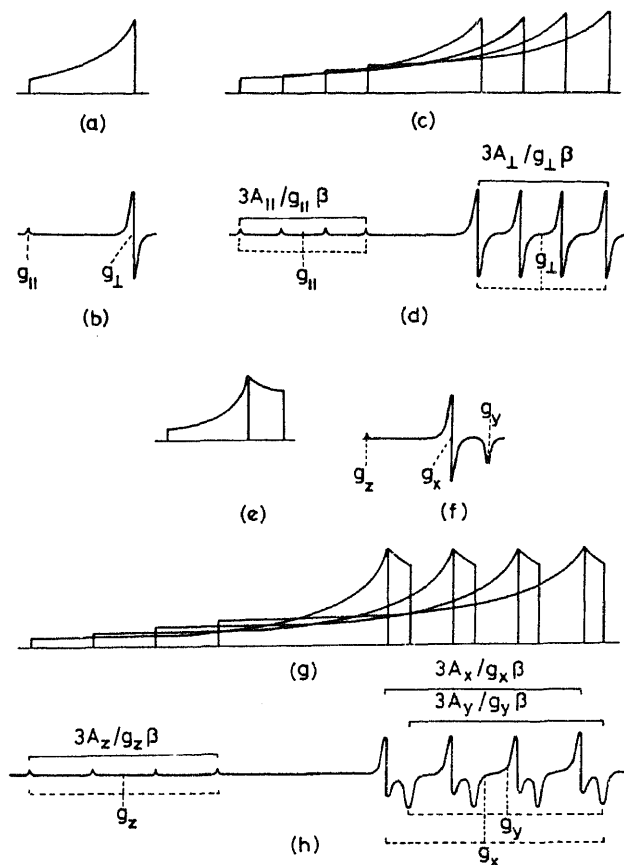


Figure 3. Typical EPR powder patterns computed for axial and non-axial g -tensor anisotropy. Parts (a)–(h) of the figure are explained in the text.

metric parameters to take account of the relative orientations of the various tensor axes. In specific instances, when the experimental lineshapes appear well-resolved, the extent of non-coincidence of the tensor axes may be reliably computed by trial-and-error lineshape simulation (Raghunathan and Sur 1984).

Powder NMR lineshape singularities similar to the EPR examples discussed above are known for quadrupolar solids. From the angular terms in (6), we see that the powder pattern will have two maxima corresponding to $\cos\theta = 0$ and $\cos^2\theta = 5/9$. The frequencies where these maxima occur are given by the resonance conditions

$$\nu'(+\frac{1}{2} \leftrightarrow -\frac{1}{2}) = \nu_0 + [\nu_Q^2/16 \nu_0] [I(I+1) - \frac{3}{4}],$$

$$\nu''(+\frac{1}{2} \leftrightarrow -\frac{1}{2}) = \nu_0 - [\nu_Q^2/9 \nu_0] [I(I+1) - \frac{3}{4}],$$

leading to the central line splitting

$$\Delta\nu = \nu' - \nu'' = [25 \nu_Q^2/144 \nu_0] [I(I+1) - \frac{3}{4}]. \quad (13)$$

Typical NMR powder patterns for the central transition in an $I = 3/2$ system in the presence of second-order quadrupolar interaction (13) are shown in figure 4 for several

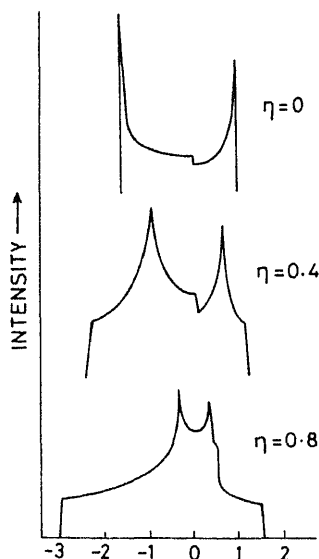


Figure 4. Typical NMR powder patterns for the central ($m_I = -\frac{1}{2} \leftrightarrow \frac{1}{2}$) transition of $I = 3/2$ nuclei in the presence of second-order quadrupolar interaction. Lineshapes computed for different η values are shown. The horizontal axis is in units of $[I(I+1) - 3/4] \nu_Q^2 / 16 \nu_0$.

values of η . In a later section, the usefulness of these lineshapes in unravelling the types of boron coordination in borate glasses is demonstrated.

In the absence of axial symmetry for the EFG, $\eta \neq 0$, and (6) is replaced by a more complicated expression involving both θ and ϕ (Taylor *et al* 1975). Such expressions have been utilised, for example, in the computer-evaluated powder pattern of ^{93}Nb NMR in powdered sodium niobate (Wolf *et al* 1970).

4. Lineshapes of amorphous materials: the need for 'random structure' models

Magnetic resonance absorption in amorphous materials is often more complicated than in crystalline powders because here we have, in addition to a distribution of 'crystallite' orientations, an inherent distribution of the spin Hamiltonian parameters. Recent reviews (Griscom 1980; Rao and Rao 1985) of the EPR of transition metal ion sites in glasses document hosts of examples where such distribution models have been invoked. In such distributed systems, the overall population is expected to be represented by a probability density function, and this basic idea has been incorporated in various recent publications.

One of the earliest, and perhaps most extreme, cases of such distributed or 'strained' spin sites was reported in some high-melting metals, where the difficulty of annealing was the cause of the strain (McCart and Barnes 1968). This had the effect of 'washing out', or causing enormous line broadening effects in the NMR quadrupolar satellite positions of ^{45}Sc , ^9Be etc. The results of this work were explained by using a simple model of random electric field gradient inhomogeneity in the usual first order treatment of quadrupolar satellites.

The idea of distributed Hamiltonian parameters has been incorporated to varying degrees in the analysis of magnetic resonance lines of vitreous inorganic and organic glasses as well. In an early investigation, Silver and Bray (1958) explained the broadening in the ^{11}B NMR line of sodium-boron oxide glasses by a 'variation in the coupling constants'. Later, Kriz and Bray (1971), in their ^{11}B NMR study of glassy B_2O_3 , reported a distribution in the boron sites which gave rise to a distribution in the quadrupole coupling constants. In a more general analysis one could, of course, take the view that random distribution exists both in the asymmetry parameters and quadrupole coupling constants.

In a very recent review, Bray (1985) has surveyed the relationship between glass structure and quadrupole or chemical shift effects in the NMR of various quadrupolar nuclei. The diagnostic guidelines provided in this survey ought to be quite useful in studies of the vitreous, glassy or amorphous quadrupolar solids. For example, the spectra to be expected for ^{11}B NMR in borate glasses may be summarised as shown in figure 5. ^{11}B in tetrahedrally bonded sites (BO_4 units) will exhibit little or no second-order quadrupolar effects because of vanishingly small EFG components, and the result is a narrow, symmetric derivative line for the $m_i = \frac{1}{2} \rightarrow -\frac{1}{2}$ transition. Symmetric BO_3 units (i.e. all bridging or all non-bridging oxygens) yield the response identified as

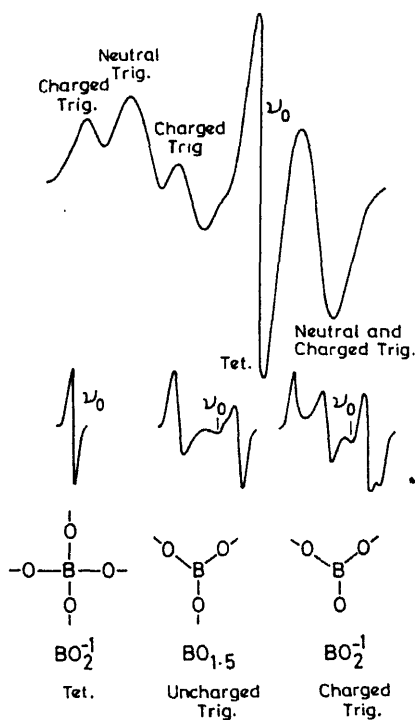


Figure 5. Computer simulation of a typical ^{11}B NMR derivative spectrum in a borate glass is shown at the top. In the middle part of the figure, the upper spectrum is decomposed into shapes corresponding to charged trigonal, neutral trigonal and tetrahedral spin sites, which are

'neutral trig' in figure 5. BO_3 units with one or two non-bridging oxygens will have a non-zero η value and will yield a spectrum marked as 'charged trig' in figure 5 (which is identifiable as one of the model lineshapes we have calculated earlier in figure 4).

In another interesting early contribution, Peterson and Kurkjian (1972) interpreted the frequency- (or field-) dependent broadenings of hyperfine structures in Ti^{3+} containing glasses by analysing the EPR lineshapes in terms of 'random glass structures', with variances (in the statistical sense) in $\vec{g}$ and $\vec{A}$. Imagawa (1968), by considering a distribution in the *single* parameter, $g_{\parallel}$, was able to obtain semiquantitative fits of the EPR spectra of Cu^{2+} in alkali borate glasses. Later on, Kawazoe *et al* (1980) have also incorporated the distribution in $g_{\parallel}$ and $A_{\parallel}$ in their simulation of the EPR of Cu^{2+} sites in silicate, borate and phosphate glasses. The authors correlate large variances in $g_{\parallel}$ with the coexistence of various borate groups 'competitively coordinating' to Cu^{2+} . By comparing the much better-resolved lineshapes of $[\text{Cu}(\text{OH})_4]^{2-}$ in DMSO-water 'glass' to the broad lines of Cu^{2+} in a $\text{PbO-B}_2\text{O}_3$ glass, they conclude that the organic glass has a rigid structure maintained by hydrogen-bonding resulting in an almost identical environment for all Cu^{2+} sites, whereas the much decreased 'rigidity' of the lead oxide glass leads to a wide distribution of Cu^{2+} sites.

The distribution of zero field parameters in Mn^{2+} -containing oxide glasses have been discussed by Kliava and Purāns (1980) and by Kliava (1982). Along somewhat analogous lines, Murai *et al* (1985) have emphasised the necessity of envisaging a $\vec{D}$ -tensor distribution in the EPR lineshape simulation of paraquinones in organic glassy matrices. Recently Hagen *et al* (1985b) have shown that paramagnetic sites in amorphous metalloenzymes have a '*g*-strain' (i.e., distributed *g*-values) and have formulated a statistical method to achieve the simulation of the corresponding EPR lineshapes. In an accompanying paper, the authors (Hagen *et al* 1985a) give a numerical procedure which is claimed to be fast in simulating the lineshapes.

The large number of results surveyed are seen to fit into a broad classification called 'random structure models' since, in almost all of the cases cited, a probability density function has to be used to get the distribution of spin Hamiltonian parameters. The density function assumed is most likely to be a normal (i.e., Gaussian) distribution, which may be univariate or multivariate with or without correlation. We note that, in the case of multivariate normal distribution, a zero correlation implies statistical independence of n variables and can be written as a product of n univariate normal distributions.

Lineshape simulations based on the distributed spin Hamiltonian parameters can be broadly classified into two categories. In the first category we find the use of both the shape function and a probability density function. Here the probability density function is used just as a weight function, and the shape function is integrated as in a simple powder case (12). The other category, proposed by Peterson *et al* (1974a), defines the magnetic resonance line as the probability density function in the magnetic field variable. This method is devoid of the use of shape function and subsequent convolution.

In Peterson's procedure, the collection of all the paramagnetic species, each with an individual geometry ω_i , is denoted by Ω . For a simple '*g*-only' case with axial symmetry, each of these ω_i can be mapped on to Euclidean three-space by a random vector $\mathbf{X}$

$g_{\perp}$, we have

$$p(g_{\parallel}, g_{\perp}, \theta) = p(g_{\parallel}, g_{\perp}) \cdot p(\theta). \quad (14)$$

$p(\theta)$ is the well known function $\sin\theta$ in the domain $\theta = 0$ to $\pi/2$. $p(g_{\parallel}, g_{\perp})$ is assumed to be a bivariate normal density function with $\sigma_{\parallel}^2$, $\sigma_{\perp}^2$ as the variances and ρ as the correlation coefficient between $g_{\parallel}$ and $g_{\perp}$. The objective is to find out the probability density function of the magnetic field from the above given densities, such that the following resonance condition is satisfied

$$h\nu = g\beta_e H = (g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2} \beta_e H. \quad (15)$$

This is achieved as follows. First the random vector $\mathbf{X}$ is transformed into a new random vector $\mathbf{Y}$ whose components are $g_{\parallel}$, $g_{\perp}$ and g . The new vector is described by the density function

$$p(g_{\parallel}, g_{\perp}, g) = p(g_{\parallel}, g_{\perp}) \cdot p(\theta) |J|, \quad (16)$$

where $|J|$ is the absolute value of the Jacobian associated with the transformation. For example, a small volume element dV_a in the first coordinate system may transform into two other volume elements dV_{b1} and dV_{b2} in the new coordinate system as shown in figure 6. After the transformation,

$$p(g_{\parallel}, g_{\perp}, g) = \frac{g p(g_{\parallel}, g_{\perp})}{[(g_{\parallel}^2 - g_{\perp}^2)(g^2 - g_{\perp}^2)]^{1/2}}. \quad (17)$$

Now the probability density of g is given by

$$p(g) = \iint p(g_{\parallel}, g_{\perp}, g) dg_{\parallel} dg_{\perp}. \quad (18)$$

The domain of this integration has to be carefully fixed because it depends on how $\mathbf{X}$ has been transformed into $\mathbf{Y}$. Peterson *et al* (1974a) suggest the evaluation of these integrals by numerical methods, e.g., Simpson's 1/3 rule with Richardson's extrapolation (see, Dahlquist and Björck 1974). In the integration, one has to avoid the singularities at $g_{\parallel} = g_{\perp}$ and $g_{\perp} = g$.

The final step in the above computation is to convert the density g into that of

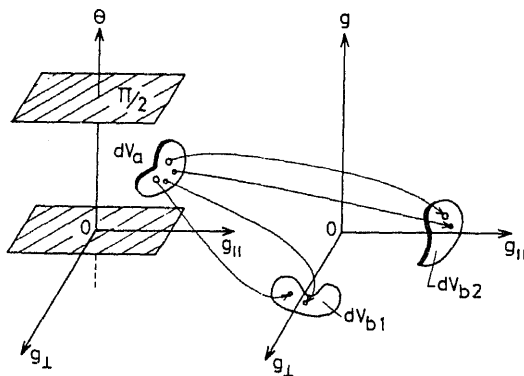


Figure 6. Coordinate transformation of domain dV_a into domains dV_{b1} and dV_{b2} .

magnetic field H as given by

$$p(H) = p(g) \cdot \left| \frac{h\nu}{\beta_e H^2} \right|, \quad (19)$$

where, once again, $h\nu/\beta_e H^2$ is the Jacobian associated with the transformation. The consequences of the g to H transformation have been well documented (Peterson *et al* 1976; Carnevale *et al* 1976). For instance, a simple re-labelling of the axis to convert the g -density into H -density may be erroneous. The last-mentioned transformation is essential for explaining the spectra recorded at different frequencies.

We have recently developed a new formalism in which all the three above-mentioned steps [viz., (i) derivation of the Jacobian and transformation of the random vector into another domain; (ii) integration of the transformed joint density to get the density of g , and (iii) transformation of the g density to H density] are automatically realised, since our computations are based on a more direct approach described in standard textbooks (see Papoulis 1965). In this approach, given the overall joint density of the random variables $x_1, x_2, \dots, x_n$ and the relation between these and a new variable z such as, say, $z = h(x_1, x_2, \dots, x_n)$, the density of z , namely, $f(z)$, is given by

$$f(z) = \frac{1}{dz} \iint_{\Delta D_z} \dots \int f(x_1, x_2, \dots, x_n) dx_1 dx_2, \dots, dx_n. \quad (20)$$

In (20), the domain of the integration, ΔD_z , is defined by the inequality

$$z < h(x_1, x_2, \dots, x_n) \leq z + dz. \quad (21)$$

Using (20), the density of H can be written as

$$p(H) = \frac{1}{dH} \iiint_{\Delta D_H} p(g_{\parallel}, g_{\perp}) \cdot p(\theta) dg_{\parallel} dg_{\perp} d\theta, \quad (22)$$

where ΔD_H is our domain of interest described by

$$H < h\nu / [(g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \beta_e] \leq H + dH. \quad (23)$$

Equation (22) is seen to be a triple-integral. The domain will have to be fixed by imposing our 'resonance condition' according to (23) as the upper and lower limits on one of the integrals. We find it easier to solve for θ given $g_{\parallel}$, $g_{\perp}$ and H (or $H + dH$). A pictorial representation of the 'domain' is given in figure 7. In this figure, for simplicity the domain involved in the evaluation of the density $p(g)$ from the densities, $p(g_{\parallel}, g_{\perp})$ and $p(\theta)$ may be considered. In analogy with (20), the appropriate expression is given by

$$p(g) = \frac{1}{dg} \iiint_{\Delta D_g} p(g_{\parallel}, g_{\perp}) p(\theta) dg_{\parallel} dg_{\perp} d\theta, \quad (24)$$

with the domain ΔD_g now being defined as

$$g < (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \leq g + dg. \quad (25)$$

The 'domain-fixing' shall now be done as follows. Referring to the concentric circles around the θ -axis at $\theta = \pi/4$ in figure 7, all the points lying outside the inner circle of

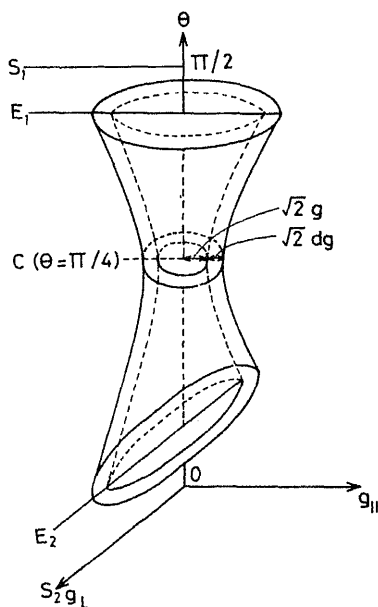


Figure 7. Pictorial representation of the integration domain ΔD_g defined by (25) in the text. The labels E_1 , E_2 , S_1 and S_2 are discussed in the text. C labels the plane of the concentric circles at $\theta = \pi/4$.

radius $\sqrt{2}g$ are seen to obey the inequality

$$g < (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}. \quad (26)$$

At the same $\theta = \pi/4$ value, all the points lying inside and on the circumference of the circle of radius $\sqrt{2}(g + dg)$ are described by the inequality:

$$(g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \leq g + dg. \quad (27)$$

We therefore see that the domain ΔD_g at $\theta = \pi/4$ is the area enclosed between the two concentric circles aforementioned. Between $\theta = \pi/4$ to $\theta = \pi/2$, figure 7 shows that the domain may be described by the area between two concentric ellipses (E_1) with a common major axis parallel to the $g_{\parallel}$ axis. Exactly at $\theta = \pi/2$, the concentric ellipses become two strips (S_1) running between $-\infty$ and $+\infty$ in the $g_{\parallel}$ direction. The breadths of the inner and outer strips are, respectively, $2g$ and $2(g + dg)$ along $g_{\perp}$, with the θ -axis passing through the centre of the strips. In the same way, we can see that between $\theta = \pi/4$ and $\theta = 0$ the domain ΔD_g is described by concentric ellipses E_2 and the strips at S_2 . But now, the strips and the (common) major axis of the ellipses are parallel to the $g_{\perp}$ axis. The points $\theta = \pi/2$ and $\theta = 0$ represent the 'singularities'.

Although a pictorial visualisation of the equivalent for $p(H)$ may be difficult, we can nevertheless write the integral as

$$p(H) = \frac{1}{dH} \int_{\theta_1}^{\theta_2} \int_{g_1}^{g_2} p(g_{\parallel}, g_{\perp}) dg_{\parallel} dg_{\perp} \int_{\theta_1}^{\theta_2} \sin \theta d\theta. \quad (28)$$

In (28) the limits for $g_{\parallel}$ and $g_{\perp}$ are fixed by truncation of $p(g_{\parallel}, g_{\perp})$ such that beyond the truncated limits (g_1, g_2 for $g_{\parallel}$ and g_3, g_4 for $g_{\perp}$) the density is negligible. After truncation, we normalize the density and carefully define the density only in the positive quadrant; that is, $g_{\parallel}$ and $g_{\perp}$ are always given as positive non-zero numbers. The upper and lower limits of θ where the resonance condition is imposed are given as

$$\theta_1 = \sin^{-1} \{ [(h\nu/\beta_e H)^2 - g_{\parallel}^2] / (g_{\perp}^2 - g_{\parallel}^2) \}^{1/2} \quad (29)$$

and

$$\theta_2 = \sin^{-1} \{ [(h\nu/\beta_e (H + dH))^2 - g_{\parallel}^2] / (g_{\perp}^2 - g_{\parallel}^2) \}^{1/2}. \quad (30)$$

We employ a Monte Carlo integration technique based on systematic sampling (Kahn 1956) to estimate the outer double integral in (28). The inner integral is the integrand for the outer double integral, for which the simple analytical solution $(-\cos\theta)$ is available. This procedure cuts down the computer time by at least one order of magnitude. We stress that our formalism is applicable with equal facility to cases where more distributed parameters have to be included (e.g., hyperfine, zero field splittings etc.). We have been able to reproduce several of the results appearing in the literature using our new formalism. A complete lineshape simulation for an experimental glass spectrum exhibiting hyperfine splittings is currently in progress.

The methodology we have described above is also useful for simulating the NMR lines by making obvious changes in the variables. In the simplest case where $\eta = 0$, either the quadrupolar coupling or the Larmor frequency, or both together, can become distributed (Peterson *et al* 1974b). Non-zero asymmetry parameters have also been considered in other simulations (Peterson *et al* 1975).

In one specific application of the density-function method, Peterson *et al* (1974a) have been able to generate the $g = 4.3$ resonance line in Fe^{3+} -containing glasses by considering the mean values 2.0 and 6.0, respectively, for $g_{\parallel}$ and $g_{\perp}$ and a large variance with negative correlation coefficient. This particular example, where a distributed single site has been predicted, is questioned by Momo *et al* (1981). The authors consider the constancy of the experimental line position with respect to temperature change as evidence against the statistically distributed model. However, it should be noted that the line position is mainly dependent on the *mean* values, whereas the width of the line is determined by variances. However, in a related paper Brodbeck (1980) concludes that in Fe^{3+} the fully rhombic crystal field limit uniquely generates the negative g -correlation required for spiking at $g = 4.3$.

Considerable caution has to be exercised in the interpretation of probability density parameters. For example, Kliava (1982) erroneously considers that, when the correlation coefficient $\rho = \pm 1$, the joint Gaussian density can be written as a product of two Gaussian densities. In fact, when $\rho = \pm 1$ the density is not well defined and has a singularity. Again, Brodbeck (1980), instead of using the complete density function description of $g_{\parallel}$ and $g_{\perp}$, simply uses the linear relationship $(g_{\parallel} - 2)/(g_{\perp} - 6) = -1$ and then uses a shape function to fit the experimental EPR curves.

5. Conclusion

their resonance parameters, present lineshape simulation procedures could often faithfully reproduce all the experimental shapes. In the amorphous or 'glassy' state, however, it often becomes necessary to view the measurable spin resonance parameters as being distributed according to a probability density function. The present probability-theory based approaches we have discussed ought to lead to reliable estimates of the statistical parameters of the distribution (such as variances and correlation coefficients). This should result in an enhanced understanding of the amorphous state of matter.

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Behaviour of acceptor states in semiconducting BaTiO_3 and SrTiO_3

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Abstract. The semiconductivity in MTiO_3 ($M = \text{Ba}, \text{Sr}$) in the temperature range of practical applications is greatly influenced by the electronic charge redistribution among the acceptor states, arising from the frozen cation vacancies as well as the transition metal ion impurities. The conductivity measurements and defect chemistry investigations above 800 K indicate that the predominant lattice defects are M - and oxygen vacancies. There is dominant p -type conduction at higher p_{O_2} values in acceptor doped materials at high temperatures. However, they are insulating solids around room temperature due to the redistribution of electrons between the neutral, singly- or doubly-ionised acceptor states. Results from EPR and resistivity measurements show that the above charge redistribution is dependent on crystal structure changes. Hence the electron or hole loss by the acceptor states is influenced by the soft modes which also accounts for the differences in electrical properties of BaTiO_3 and SrTiO_3 . The results are also useful in explaining the positive temperature coefficient in resistance and some photo-electrochemical properties of these solids.

Keywords. BaTiO_3 ; SrTiO_3 ; semiconductivity in perovskites; acceptor states.

1. Introduction

Semiconducting MTiO_3 ($M = \text{Ba}, \text{Sr}$) perovskites find applications in positive temperature coefficient resistors (PTCR), grain-boundary and intergranular layer capacitors, electrodes for photoelectrochemical reactions and photochromic devices. The electrical conductivity of these solids in the temperature range of practical applications has peculiar variations. For example, around the Curie point (T_c), the electrical resistivity of n -type BaTiO_3 ceramics increases with temperature by several orders of magnitude. Another case is of SrTiO_3 annealed in a H_2 -atmosphere, whose resistivity increases with temperature (metallic behaviour) whereas the donor-doped SrTiO_3 exhibits decreasing resistivity with temperature (semiconductor behaviour). These diverse features arise from the behaviour of acceptor states in MTiO_3 , which are caused by cation vacancies in the M -sublattice or the impurities, particularly the $3d$ metal ions. It is possible that either (i) the concentrations of the atomic defects formed at high temperatures (of crystal growth or sintering) remain frozen and the electronic (charge) equilibrium is readjusted or (ii) the defects remain in equilibrium with the surroundings all through the cooling history. Our observations indicate that possibility (i) is to be preferred. The present investigations confirm the redistribution of charges between neutral, singly- or doubly-ionised defects, being controlled by crystal structure changes and hence, influenced by the soft modes.

2. The conduction mechanism

Thus the conduction electron corresponds to Ti^{3+} and the positive hole to $\text{O}^- \cdot M\text{TiO}_3$ can be made an n -type conductor either by doping with donors or by annealing in an atmosphere of lower oxygen partial pressure (p_{O_2}) above 800 K. *Donor* denotes any impurity with the nominal ionic charge more than that of the lattice sites it substitutes (La^{3+} at M^{2+} or Nb^{5+} at Ti^{4+} sites). The charge compensation of the donor in $M\text{TiO}_3$ can be by electron (e') in the conduction band (electron compensation), cation vacancy (vacancy compensation) or acceptor impurity (impurity compensation). *Acceptor* denotes the dopant having a lower valence than the replacing ion (Na^+ at M^{2+} or Fe^{3+} at Ti^{4+} sites). The acceptor is charge compensated by a positive hole (h'), oxygen vacancy or donor impurity. More than one type of compensation is possible simultaneously. At higher p_{O_2} , electron or hole compensation alone leads to change in electrical conductivity. At lower p_{O_2} , the oxygen vacancies formed can ionise, leading to electrons in the conduction band. Although a given metal ion impurity can occupy both the M^{2+} and Ti^{4+} sites and hence can act as donor and acceptor simultaneously, the substitution is mostly guided by ionic radii as well as the crystal field energy.

The nature of the charge carriers in n -type $M\text{TiO}_3$ continues to be debated, whether they are small polarons or band electrons. The electrical and optical properties can be interpreted either way (Ihrig and Hennings 1978). The presence of a conductivity-dependent optical absorption maximum around 0.6 eV (Berglund and Braun 1967) favours the small polaron concept. However, the drift mobility of 0.1–0.5 $\text{cm}^2/\text{V sec}$ in BaTiO_3 (Seuter 1974) and 3.3–8.0 $\text{cm}^2/\text{V sec}$ in SrTiO_3 is too high for thermally activated small polaron hopping. This together with the fact that the drift and the Hall mobilities are the same, support the band conduction. From the extensive discussions available in literature, it seems that the electrical properties of $M\text{TiO}_3$ cannot be explained by electrical experiments alone, and that the nature of the charge carriers has to be interpreted in the context of optical and electrical measurements, defect chemistry investigations and chemical analyses. All these data support the small polaron model with negligibly small or even negative kinetic transport terms and low donor dissociation energy of ≈ 0.1 eV. The enhanced mobility is due to the correlation of successive polaron hops. It can be considered that conduction in $M\text{TiO}_3$ comes close to the so-called 'transition region' between the validity of the adiabatic and nonadiabatic theories.

3. Defect chemistry

Since the acceptor states arise from the lattice defects, it is necessary to present some facts regarding conductivity behaviour and defect chemistry of $M\text{TiO}_3$ above 800 K and try to extrapolate them to lower temperatures.

Figure 1 shows the high temperature conductivity of undoped, donor- as well as acceptor-doped BaTiO_3 as functions of equilibrium p_{O_2} values. It is evident from the figure that undoped BaTiO_3 is a p -type conductor at $p_{\text{O}_2} > 10^{-5}$ atm whereas it is an n -type at lower p_{O_2} . Away from the conductance minimum, a linear relation,

$$\log \sigma = (1/m) \log p_{\text{O}_2}, \quad (1)$$

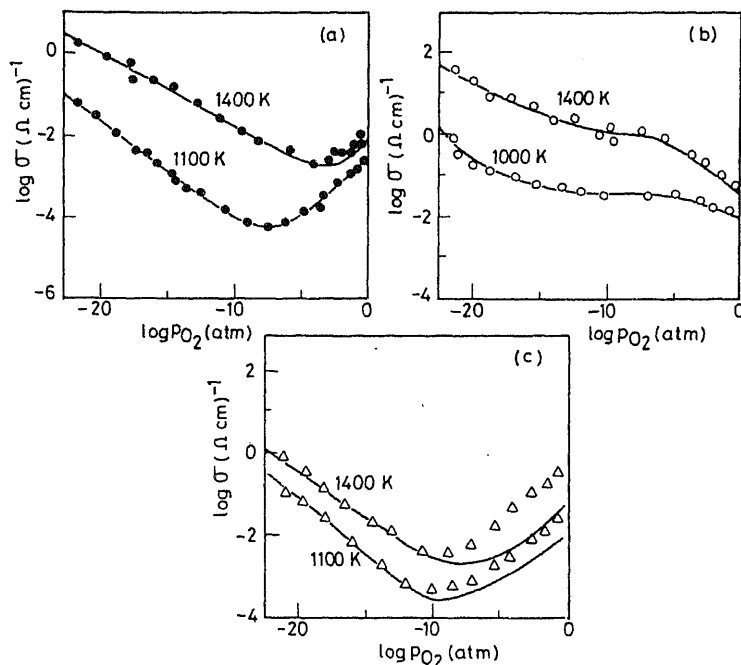


Figure 1. Electrical conductivity of BaTiO_3 as a function of equilibrium p_{O_2} at different temperatures (a) undoped, (b) doped with 0.3 at % donor (c) doped with 0.3 at % acceptor. The individual points are the experimental values. The full lines are calculated from the model explained in the text.

distinguished on the curves in figure 1b: increase in conductivity with falling p_{O_2} (region 1), followed by the p_{O_2} -independent conductivity (region 2) and further increase at very low p_{O_2} (region 3). This behaviour is indicative of three independent mechanisms operating in different p_{O_2} regions. The shape of the conductivity curve is different for donor-doped specimens equilibrated below 1400 K (figure 1b). Incorporation of acceptors shifts the conductivity minimum to lower p_{O_2} and enhances the p -type conductivity at $p_{\text{O}_2} > 10^{-6}$ atm. Thus the conductance behaviour at higher temperatures (figure 1c) clearly indicates that the acceptor impurities are dissolved in the bulk of the specimen. Around room temperature, the acceptor-doped specimens are very insulating and p -type conductivity has never been observed in these samples. This led to the hypothesis that the acceptor dopants do not dissolve in the bulk of the grains but segregate preferentially at the grain boundaries (Heywang 1971; Brauer 1974).

The above results can be explained on the basis of the defect chemistry of BaTiO_3 , with the following simplifications. The defects due to interstitial atoms can be excluded on account of the close-packed structure of the lattice. Because the Ti^{4+} ion is placed in a deep potential minimum and a high valence is associated with it, the existence of Ti^{4+} on the lattice is not affected. For the first step, we consider the effect of

V'_{Ba} , V''_{Ba}) vacancies. The electroneutrality can be represented as

$$n + [V'_M] + 2[V''_M] + [A'] + 2[A''] = p + [V'_O] + 2[V''_O] + [D'] + 2[D''], \quad (2)$$

where $[A]$, $[A']$, $[D']$ and $[D'']$ are the concentrations of the singly- or doubly-ionised acceptor or donor impurities, n and p are the concentrations of electrons and holes respectively.

Above 800 K, the concentration of oxygen vacancies varies with p_{O_2} and temperature, in accordance with the reaction,



where $O_{O^{2-}}$ = oxygen in the regular lattice sites, and O_2 = oxygen molecule in the gas phase. From the law of mass action, it follows that,

$$[V_{O^{2-}}]n^2 = K_0 e^{-E_0/kT} p_{O_2}^{-1/2}, \quad (4)$$

with E_0 = the energy of formation of $V_{O^{2-}}$, k = Boltzmann constant and K_0 = the preexponential factor. Due to their extremely low diffusion coefficient, the Ba-vacancies are in equilibrium with the surroundings only above 1400 K, involving the modified Schottky relation:

$$[V''_{Ba}][V_{O^{2-}}] = K_s e^{-E_s/kT}, \quad (5)$$

where K_s is the preexponential factor and E_s , the activation energy for the reaction occurring at the grainboundary layer, leading to the generation of most of the Ba-vacancies (Wernicke 1976):



where $Ba_{lattice}$ and $O_{lattice}$ are from the regular lattice positions of $BaTiO_3$.

Besides the 3d metal ion impurities, one encounters Ba-vacancies as acceptors being frozen-in below 1400 K due to the low diffusion coefficient. The acceptors are characterised by their ionisation energy. It follows from the band theory that the acceptors occupy suitable positions in the forbidden gap and obey the Fermi statistics so that,

$$[A^0] = [A] / \{ 1 + \frac{1}{2} e^{(E_f - E)/kT} + e^{(2E_f - E' - E'')/kT} \}, \quad (7)$$

$$[A'] = \frac{1}{2} [A^0] e^{(E_f - E')/kT}, \quad (8)$$

$$[A''] = [A^0] e^{(2E_f - E' - E'')/kT}, \quad (9)$$

where $[A]$ = total concentrations of the acceptors (Ba-vacancies and impurities);

$[A^0]$ = the concentration of neutral acceptors;

E' , E'' = the energy levels of singly- and doubly-ionised acceptors;

E_f = Fermi energy.

Besides ionic defects, one has to also consider the concentrations of electrons and holes:

$$n = N_c e^{-(E_c - E_f)/kT}, \quad (10)$$

$$p = N_v e^{-(E_f - E_v)/kT}, \quad (11)$$

where N_c and N_v are the density of states in the conduction and valence band respectively; E_v and E_c are the upper limit of valence band and lower limit of conduction band respectively.

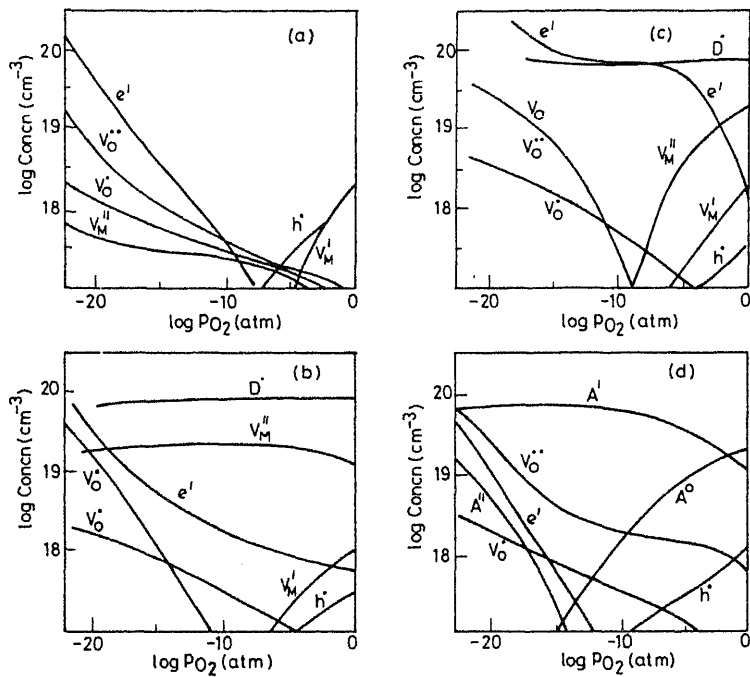


Figure 2. Calculated defect concentration as a function of p_{O_2} for (a) undoped $BaTiO_3$ equilibrated at 1400 K (b) doped with 0.3 % donor equilibrated at 1100 K (c) doped with 0.3 % donor equilibrated at 1400 K and (d) doped with 0.3 atom % acceptor equilibrated at 1400 K.

The unknown concentrations of the neutral and ionised defects can be calculated if a proper choice of the material parameters (E' , E'' , K_0 , E_0 etc.) are made in the light of reliable experimental points and with the assumption that electroneutrality of the solid, as per equation (2), is preserved. Setting up simultaneous equations from (2), (4) and (7)–(11), one can numerically solve for the concentrations of various defects at selected temperature and p_{O_2} and relate them to conductivity:

$$\sigma = e(n\mu_n + p\mu_p), \quad (12)$$

where μ_n and μ_p are the mobilities of electrons and holes available from Seuter (1974). The full lines in figure 1a–c are obtained by this procedure. The deviations of the calculated values from the experimental points are more on the p -type side, particularly for the acceptor-doped $BaTiO_3$.

Figure 2 shows the p_{O_2} -dependence of defect concentrations for $BaTiO_3$ at higher temperatures. Accordingly, the electroneutrality for the undoped $BaTiO_3$ can be simplified as:

$$[V'_A] = p, \text{ at } p_{O_2} > 10^{-5} \text{ atm}$$

and $n = [V'_O] + 2[V''_O]$ at lower p_{O_2} , which accounts for the p -type behaviour changing over to n -type as p_{O_2} is lowered. For donor-doped $BaTiO_3$, the electroneutrality relation can be simplified as:

$n = [D^\cdot] - [A''] - 2[A'']$ in region 1, $n = [D^\cdot]$ in region 2, and $n = [V_O^\cdot] + 2[V_O^{\cdot\cdot}]$ in region 3, so that n -type conductance prevails throughout the p_{O_2} range.

For the acceptor doped $BaTiO_3$,

$$p = [V_O^\cdot] + 2[V_O^{\cdot\cdot}] - [A'] \text{ at } p_{O_2} > 10^{-9} \text{ atm}$$

and $n = [V_O^\cdot] + 2[V_O^{\cdot\cdot}] - [A'] + [A'']$ at lower p_{O_2} values. However, the significant point in figure 2c is the existence of larger concentrations of neutral acceptors at higher p_{O_2} .

Very similar results, as above, are obtained for the defect chemistry of $SrTiO_3$ as well.

The prediction of conductivity behaviour at lower temperatures, using the materials parameters from high temperatures has to involve a number of assumptions. Below 1400 K, the Ba-vacancies and below 800 K the oxygen vacancies are no more in equilibrium with the surroundings. Therefore, at lower temperatures, the concentration of the atomic defects are frozen whereas the electronic equilibria will readjust so that,

$$[V_O] = [V_O^\cdot] + [V_O^{\cdot\cdot}] = \text{a constant}, \quad (13)$$

$$[V_{Ba}] = [V_{Ba}^0] + [V_{Ba}^{\cdot}] + [V_{Ba}^{\cdot\cdot}] = \text{a constant}, \quad (14)$$

where $[V_O]$ and $[V_{Ba}]$ are the total concentrations of the corresponding vacancies.

No details of these charge readjustments are known except that the empty levels in the band gap are successively filled with electrons from bottom upwards. Using (7)–(11) and assuming the constancy of total atomic defects as in (13) and (14), one can calculate the temperature dependence of conductivity, provided one assumes that the donor is

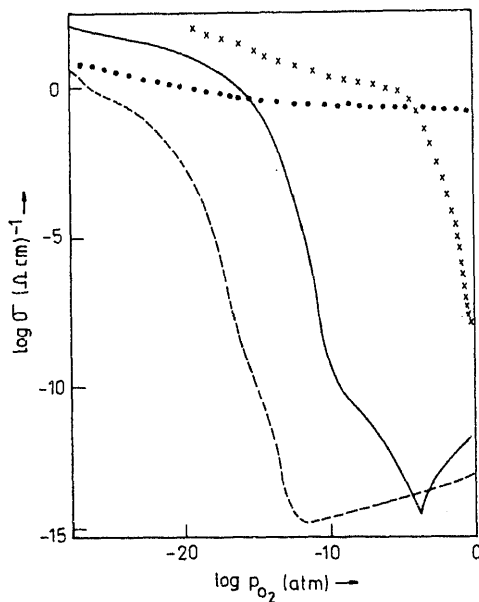


Figure 3. Calculated electrical conductance of $BaTiO_3$ at 300 K, using high temperature parameters; (—) undoped; ($\times \times \times$) donor doped, equilibrated at 1400 K; (...) donor doped and equilibrated at 1100 K; (---) acceptor doped and equilibrated at 1400 K.

where $[D^{\cdot}]$ = concentration of singly-ionised donor and $E_D^{\cdot}$ = energy of the donor levels.

Figure 3 shows the conductivity of BaTiO_3 at 300 K as a function of p_{O_2} . The n - and p -type regions are noticeable in undoped and acceptor-doped BaTiO_3 with extremely low conductivity values. Donor-doped BaTiO_3 equilibrated at 1400 K has lower conductivity than the sample equilibrated at 1100 K. The experimental observations show that the room temperature conductivity is dependent on the rate of cooling from the sintering temperature (~ 1600 K). When cooled at moderate rates (50–150 K/hr), the samples are conducting ($\sigma \approx 0.1 \text{ ohm}^{-1} \text{ cm}^{-1}$) whereas at a 2–10 K/hr cooling rate the samples are insulating ($\sigma \leq 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$). This is not in accordance with the prediction from defect chemistry, which also indicates similar behaviour for SrTiO_3 . Experimentally one observes that donor-doped SrTiO_3 when sintered in air is insulating, irrespective of the cooling rates. It is, therefore, obvious that the nature of charge redistribution between the various acceptor states is not identical and hence, the low temperature electroneutrality relations have to be modified.

4. EPR and resistivity results

The electronic redistribution between the acceptor type defect states can be followed by electron paramagnetic resonance (EPR). BaTiO_3 as such showed no EPR spectrum at any temperature of measurement (80–500 K) indicating very low concentrations of paramagnetic impurities. Donor-doped BaTiO_3 , sintered in air at 1650 K, showed an asymmetric signal of $g = 1.963$ and a very weak signal of $g = 1.997$ at 300 K (figure 4). The weak $g = 1.997$ signal is absent when no extra TiO_2 is added (usually ~ 0.5 mole %) as the sintering additive. Above the Curie point ($T_c \approx 398$ K), the $g = 1.997$ signal acquires pronounced gain in intensity, whereas the $g = 1.963$ signal becomes more symmetric with no difference in intensity. In the case of BaTiO_3 annealed at $p_{\text{O}_2} \approx 10^{-20}$ atm and 1200 K, only the $g = 1.963$ signal is observed at 300 K, while the $g = 1.997$ appears above T_c with much lower intensity than that of the donor-doped specimens. We have identified that the $g = 1.963$ signal originates from the $\text{Ti}^{3+} - V_{\text{O}}$ defect complex whereas $g = 1.997$ arises from singly ionised V'_{Ba} (Kutty *et al* 1984). In the tetragonal phase, the Ba-vacancies are either neutral or doubly ionised (V''_{Ba} , He-like) and hence, do not show EPR signals. If V''_{Ba} were present in the tetragonal phase, the conversion to V'_{Ba} ($V''_{\text{Ba}} = V'_{\text{Ba}} + e'$) should enhance the conduction. Since the reverse is the case (figure 5), neutral V_{Ba} should be the right choice. The appearance of the $g = 1.997$ signal is reversible across the phase transition. Its disappearance in the tetragonal phase may be related to the crystal structure changes or due to the existence of spontaneous polarisation. The EPR spectra recorded at lower temperatures indicate that $g = 1.997$ acquires intensity in the rhombohedral phase as well (figure 6). Since the rhombohedral phase is also ferroelectric, the appearance of the $g = 1.997$ signal depends on the crystal structure changes and not on the spontaneous polarisation. Considering the difference in intensity of the $g = 1.997$ signal in donor-doped BaTiO_3 when compared to that of

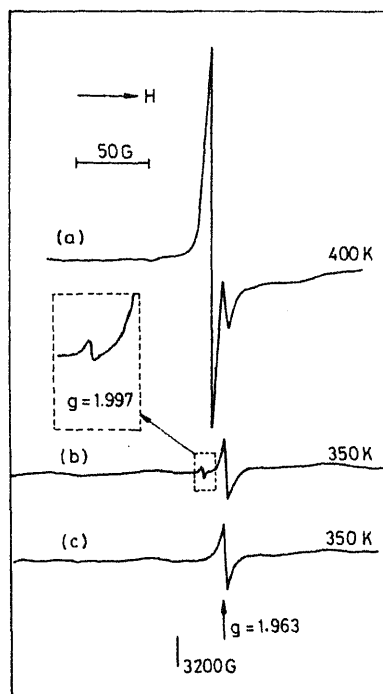


Figure 4. EPR signals of La-doped BaTiO_3 (a) at 400 K, (b) at 350 K and (c) BaTiO_3 sample annealed at $p_{\text{O}_2} \sim 10^{-20}$ atm and 1200 K.

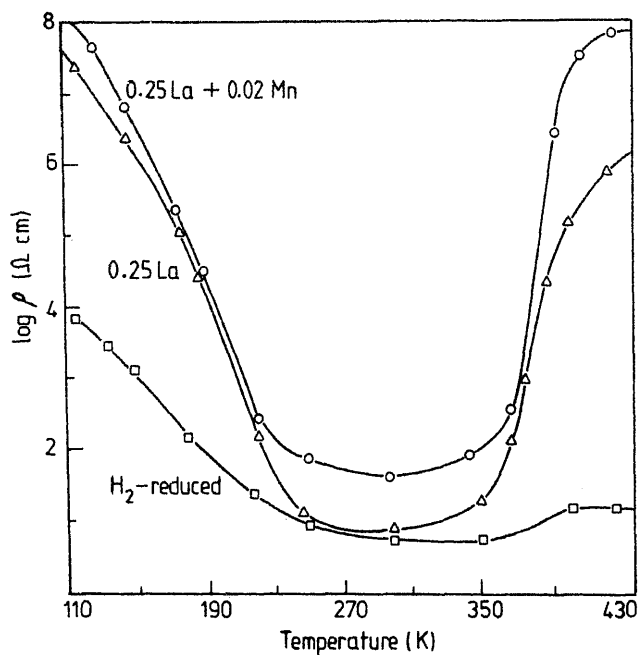


Figure 5. Electrical resistivity of La-doped as well as H_2 -annealed BaTiO_3 .

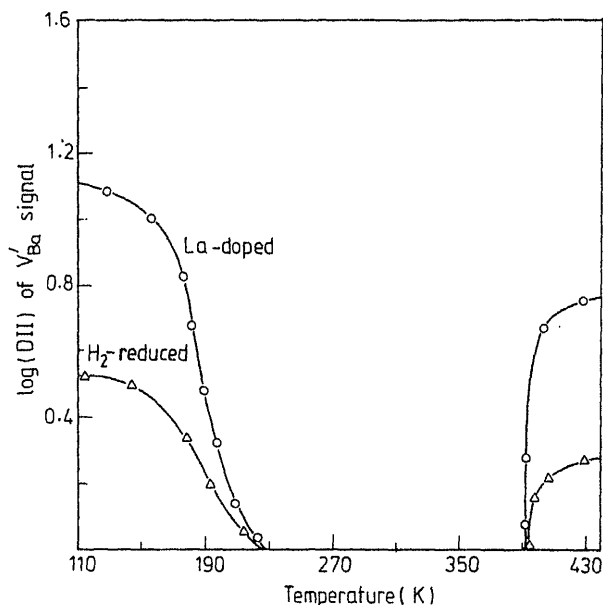


Figure 6. Variation in intensity of V'_{Ba} EPR signal for La-doped as well as H_2 -annealed BaTiO_3 .

BaTiO_3 annealed in low p_{O_2} , it can be concluded that the concentration of V_{Ba} is very much higher in donor-doped materials.

Corresponding changes in electrical resistivity (figure 5) indicate that the Ba-vacancies are neutral in tetragonal and orthorhombic phases whereas they are singly ionised in the cubic and rhombohedral phases. The change over of $V_{Ba} + e' \rightleftharpoons V'_{Ba}$ leads to the trapping of charge carriers which are therefore not available for conduction and hence increase in electrical resistivity. These observations lead to a new explanation for the PTCR effect in BaTiO_3 ceramics (Kutty *et al* 1985). Although the sign of the temperature coefficient of resistivity across the rhombohedral-orthorhombic phase transition is in accordance with that for any semiconductor, the magnitude of resistivity change is large in a short temperature interval and probably arises from the charge redistribution between the acceptor states arising from Ba-vacancies. It is evident from figures 5 and 6 that V'_{Ba} has higher stability in the cubic as well as the rhombohedral phases.

It is known that 3d-metal ions in concentrations < 0.1 atom %, enhance the PTCR property and improve the grain-boundary layer capacitance (Brauer 1974; Ueoka 1974). At higher concentration ranges, 3d-ions enhance the resistivity of BaTiO_3 even when sintered at lower p_{O_2} atmospheres. The magnetic susceptibility measurements of such samples showed that the valencies of Cr, Mn, Co dopants change with p_{O_2} , whereas that of Fe, Ni, Zn remain unchanged (Hagemann and Ihrig 1979). Therefore the nature of Mn and Fe at concentrations < 0.1 atom % in BaTiO_3 has been investigated. Mn

spectrum with $g = 2.0024$ and hyperfine splitting constant $A = 80 \times 10^{-4} \text{ cm}^{-1}$ is noticed. This spectrum is identified as that arising from the $|\frac{1}{2} M_I\rangle \rightarrow |-\frac{1}{2} M_I\rangle$ transition of Mn^{2+} occupying Ti^4 sites (Kutty and Murugaraj 1985). The appearance of the 6-line Mn^{2+} signal is reversible across the phase transformation. When recorded at lower temperatures, the Mn^{2+} -signal appears only in the rhombohedral phase. Figure 7 shows that the Mn^{2+} signal is not observed in the orthorhombic and tetragonal phases. When the concentration of Mn is increased to 0.05 atom %, two sets of signals of $g = 2.0024$ and 2.0028 are observed with low intensity in these two phases. Above T_c only one set of 6-line signal is noticed with $g = 2.0024$ and 100-fold increase in intensity (figure 7). The two sets of 6-line signals arise from the anisotropy of the g -factor in the tetragonal phase. The EPR of BaTiO_3 : 0.02 atom % Mn reduced in H_2 shows the same temperature variation features as those of BaTiO_3 : 0.25 La, 0.02 Mn sintered in air. When BaTiO_3 : 0.05 atom % Mn is annealed in O_2 at 1200 K, no signal from Mn is noticed in all the phases of BaTiO_3 .

The EPR of Mn^{4+} ions is observed at room temperature in SrTiO_3 , TiO_2 and PbTiO_3 indicating a larger relaxation time for this d^3 -ion (Müller 1959; Anderson 1960; Hennings and Pomplun 1974). There is no reason why Mn^{4+} should have a shorter relaxation time in BaTiO_3 at room temperature. Obviously, Mn does not exist in the tetravalent state, whereas Mn^{3+} (d^4) with its short relaxation time should be the species whose EPR signal can be observed only at very low temperatures ($\sim 10 \text{ K}$). Therefore, the absence of a Mn signal in the tetragonal and orthorhombic BaTiO_3 can be attributed to the existence of Mn as Mn^{3+} ions. For the same sample, Mn exists as Mn^{2+} in the cubic and rhombohedral phases indicative of the crystal-structure-dependent $\text{Mn}^{3+} + e' \rightleftharpoons \text{Mn}^{2+}$ conversion, whereby Mn^{3+} traps electrons and augments the effect of $V_{\text{Ba}} + e' \rightleftharpoons V'_{\text{Ba}}$ in lowering the number of charge carriers. This

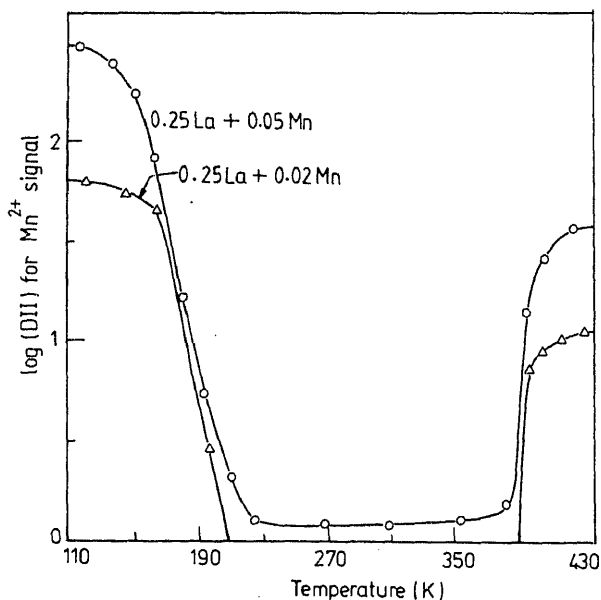
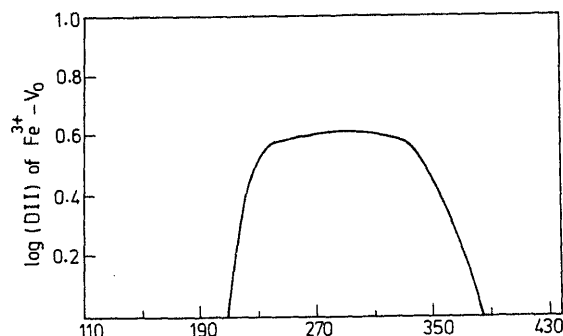


Figure 7. Change in intensity of Mn^{2+} EPR signal for various concentrations of Mn in La-doped BaTiO_3 .

leads to enhanced resistivity jump around the two-phase transition temperatures (figure 5).

Incorporation of 0.01–0.1 atom % Fe^{3+} ions in BaTiO_3 also enhances the PTCR effect but to a lesser extent than that of Mn. EPR spectrum of $\text{BaTiO}_3:0.25 \text{ La}, 0.01 \text{ Fe}^{3+}$ showed two additional signals of $g = 5.542$ and 11.831 which are identified as arising from the anisotropic g -factor components of $\text{Fe}^{3+}-V_{\text{O}}$ defect complex in the tetragonal phase (Murugaraj and Kutty 1986). When the concentration of Fe^{3+} is increased to 0.05 atom %, an additional signal of $g \approx 2.00$ is observed at 300 K which originates from $\text{Fe}_{\text{Ti}}^{3+}$. In the orthorhombic phase, there are three signals of $g = 4.437, 5.54$ and 11.831 due to the non-equivalence of the $\text{Fe}^{3+}-V_{\text{O}}$ defect complex. The temperature variation of the combined intensities of $\text{Fe}^{3+}-V_{\text{O}}$ signals is shown in figure 8. The signals vanish as the temperature approaches T_c , as does the orthorhombic-rhombohedral transition at low temperatures. This may either correspond to the dissociation of $\text{Fe}^{3+}-V_{\text{O}}$ or the capture of an electron to form $\text{Fe}^{3+}-V_{\text{O}}(e')$, whereby the five unpaired electrons of the high spin Fe^{3+} may couple with the captured electron at the oxygen vacancy to an effective even-spin state, and hence not observable by EPR. If thermal dissociation is the cause, there is no reason why the signals should vanish in the low temperature rhombohedral phase. Further, optical illumination with blue light does not affect $\text{Fe}^{3+}-V_{\text{O}}$ signals and hence does not involve other oxidation states of Fe (Berney and Cowan 1981). Therefore, the disappearance of these signals is due to the formation of $\text{Fe}^{3+}-V_{\text{O}}(e')$. It has been shown that the Fe^{3+} ion moves towards the oxygen vacancy of the defect complex which reduces the rotation of the $\text{Fe}^{3+}-V_{\text{O}}$ centre by 1.6 times as compared to the intrinsic value for TiO_6 octahedra (Müller 1981). Since the coordination polyhedra are nearly undistorted in the rhombohedral BaTiO_3 , the structural changes across T_c are identical to those of a orthorhombic-rhombohedral transition.

With SrTiO_3 , the EPR signals arising from V'_{Sr} and Mn^{2+} are observable at room temperature (figure 9) which is in agreement with the results from cubic BaTiO_3 . However Mn shows more complicated EPR spectrum. Oxygen annealed $\text{SrTiO}_3:0.01 \text{ atom \% Mn}$ shows the 6-line signal of $g = 1.997$ arising from Mn^{4+} (Müller 1959). When the same is reduced in H_2 , other signals arising from Mn^{2+} ($g = 2.0024$) and $\text{Mn}^{2+}-V_{\text{O}}$ ($g = 2.001$) are noticed. As the reduction temperature is increased, the Mn^{4+}



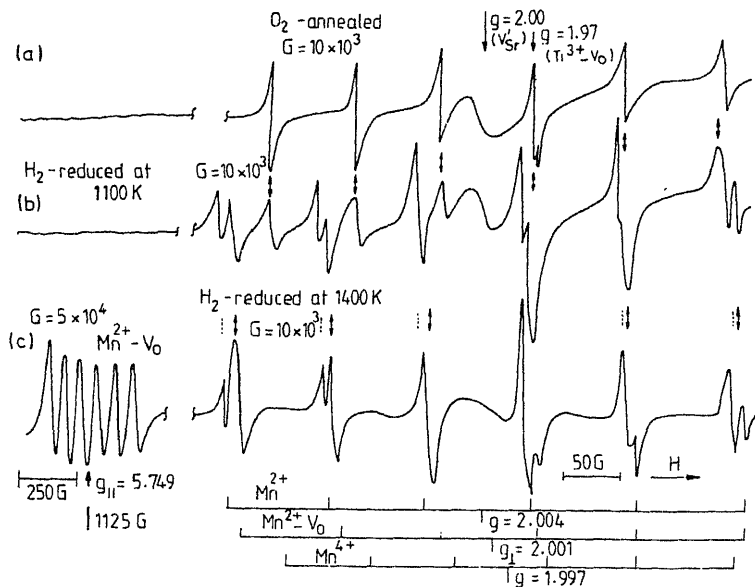


Figure 9. EPR spectra of SrTiO_3 doped with 0.01 atom % Mn and annealed at different conditions.

signal vanishes and the intensity of the $\text{Mn}^{2+}-V_{\text{O}}$ signal increases. The identity of $\text{Mn}^{2+}-V_{\text{O}}$ is further confirmed by the fact that the $g_{\parallel}$ component ($= 5.749$) appears in the deeply reduced samples. Figure 10 shows the variation in intensity of these signals with temperature. The intensity of V'_{Sr} signal of SrTiO_3 annealed at 1400 K, increases with temperature. Around the cubic-tetragonal phase transition (~ 108 K), the intensity increases and at lower temperature it falls off. Whereas the intensities of Mn^{4+}

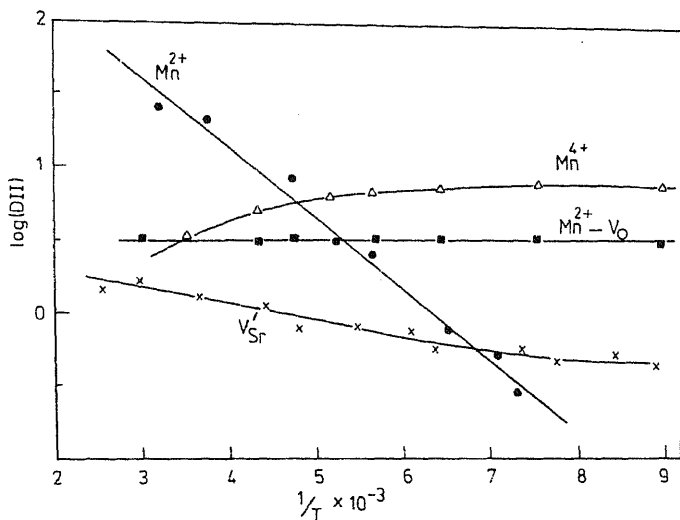


Figure 10. Variation in intensity of the various signals in SrTiO_3 with temperature.

and $Mn^{3+} \rightarrow O$ signals remain nearly unchanged, that of Mn^{2+} continuously decreases with lowering temperature. The Mn^{2+} signal vanishes around 108 K. The decrease in intensity of the Mn^{2+} signal is not accompanied by line broadening since the half-band width remains unchanged all through the observed temperature range. Therefore the disappearance of the Mn^{2+} signal cannot be due to change in the rotational order parameter but is due to a change in the valence state as in the case of $BaTiO_3$ except that the $Mn^{2+} \rightleftharpoons Mn^{3+} + e'$ conversion occurs continuously as the temperature is lowered. From the slope of the $\log I_{Mn^{2+}}$ vs $1/T$ curve (figure 10) the activation energy is found to be ~ 0.065 eV which corresponds to one of the transverse optical (TO) soft modes of $SrTiO_3$ (Servain *et al* 1980). Optical illumination (infrared) does not affect the EPR signals at low temperature, possibly due to the fact that the frequency of the corresponding vibrations is not coincident with that of some point on the dispersion curve and hence cannot be transmitted underdamped.

The resistivity of $SrTiO_3$ reduced at $p_{O_2} \approx 10^{-20}$ atm and 1400 K increases with temperature (figure 11), whereas those of $SrTiO_3$ samples annealed at $p_{O_2} 10^{-10}$ atm and 1100 K show the usual semiconductor behaviour. Around the cubic-tetragonal transition temperature, the resistivity of the deeply reduced samples shows reversal in temperature coefficient. The correlation in temperature variations of EPR signals of the acceptor centres and the resistivity indicates that the metallic behaviour arises from the increased trapping of electrons at the defect sites. It can be inferred, therefore, that the charge redistribution between the various acceptor states in $SrTiO_3$ is different from that observed in $BaTiO_3$. The underdamped soft modes of $SrTiO_3$ may facilitate continuous redistribution at structurally favourable acceptor centres.

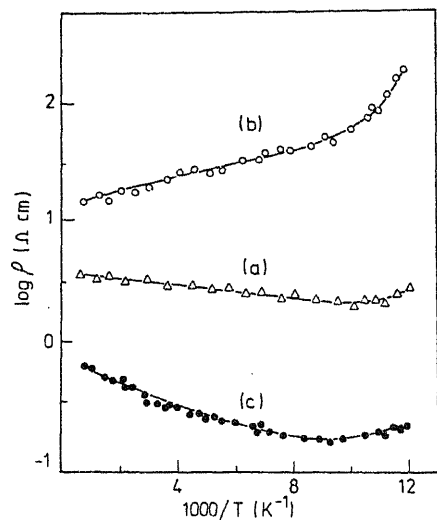


Figure 11. The electrical resistivity of $SrTiO_3$ (a) annealed at $p_{O_2} \sim 10^{-20}$ atm and 1400 K; (b) annealed at $p_{O_2} \sim 10^{-10}$ atm and 1100 K, (c) $SrTiO_3$ single crystal annealed at $p_{O_2} \sim 10^{-20}$ atm and 1400 K.

5. Photoelectrochemical properties

The junction between the semiconducting SrTiO_3 or BaTiO_3 and aqueous redox systems shows photon-assisted electric current when illuminated with light of band gap energy. However, BaTiO_3 electrodes show response to visible light of lesser intensity than when illuminated with UV, which is attributed to the existence of sub-band gap states in the forbidden gap (Chang *et al* 1983) (figure 12), whereas no visible light response is observed for SrTiO_3 . The flat band (f.b.) potential (V_{fb}) for BaTiO_3 doped with La is ≈ -0.85 V (vs SCE) in the UV and the apparent flat band potential (V'_{fb}) in the visible is ≈ -0.5 V. Therefore the mid-band gap state should be located around 0.28 V ($V_{fb} - V'_{fb}$) below the Fermi level. This mid-band gap cannot arise from acceptor type centres whereas they arise from donor-type states which may arise from $\text{Ti}^{3+}-V_O$ centres. Since the Fermi level in BaTiO_3 itself is located ~ 0.3 eV below the conduction band edge (Butler *et al* 1981), the $\text{Ti}^{3+}-V_O$ sub-band should be located around 0.6 eV below the conduction band. This energy value coincides with that of the broad absorption maximum noticed in the infrared region for donor doped BaTiO_3 and whose intensity increases with conductivity (Berglund and Braun 1967).

The difference in photoresponse between the tetragonal BaTiO_3 and cubic SrTiO_3 has been explained on the basis of a band model (figure 13) (Kutty and Gomathidevi 1985). The cation vacancies disrupt the chemical bonds with oxygen and thereby perturb the filled valence band (made of the $2p^6$ orbitals of O^{2-} ions) creating acceptor states. If these states are not lifted out of the valence band, they will remain neutral. In the cubic phase, due to crystal structure changes, the whole of the V_{Ba} acceptor states are lifted out of the valence band so as to form discrete levels within the band gap and can capture electrons from the conduction band to become V'_{Ba} . This will happen around T_c for BaTiO_3 whereas for SrTiO_3 the ionised acceptor states exist at room temperature itself. Correspondingly, the electronic states of other acceptors are also affected in the two phases. The electrons are photoexcited from the valence band to the $\text{Ti}^{3+}-V_O$ sub-band from where they will tunnel into the conduction band. The photogenerated holes may travel uphill, finding their way into neutral V_{Ba} states and will be available at the

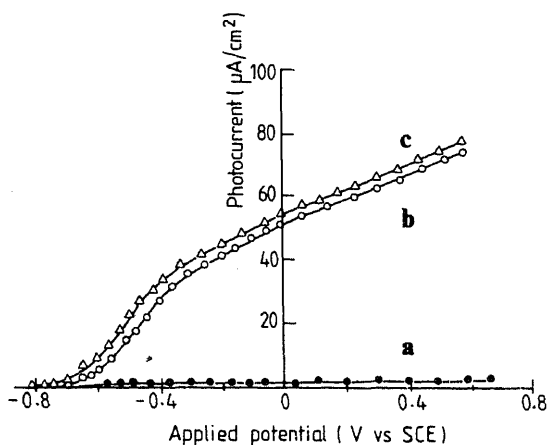


Figure 12. Visible light photocurrent vs applied potential for (a) SrTiO_3 ; (b) H_2 annealed

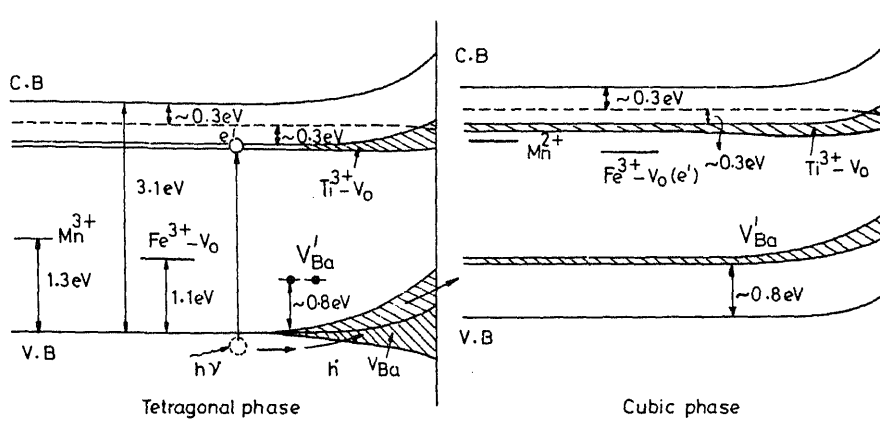


Figure 13. Schematic changes in energy level for tetragonal and cubic phases of BaTiO_3 . Possible energy levels of Mn and $\text{Fe}^{3+}-V_O$ are also shown.

interface in response to the depletion layer. In the cubic phase, mobility of photogenerated holes into the V'_{Ba} states is restricted and hence the difference in response to visible light.

6. Discussion

The results indicate that charge redistribution among the acceptor states takes place at lower temperatures and is dependent on the structural changes in the lattice. The results also demonstrate that the same impurity can be present in more than one type of defect centre so that the shift from insulating to conducting state cannot be accounted for in terms of the concentrations of acceptor and donor simultaneously present. The charge redistribution of the acceptor can be represented by one of the two alternatives:

$$\text{hole loss: } A \rightleftharpoons A' + h^+$$

$$\text{electron loss: } A'' \rightleftharpoons A' + e'$$

(16)

These boundary limits are functions of the electronic deformation and polarization energy, E_{dp} as well as the electron affinity of the bulk crystal, E_A . Additionally, if the acceptors are transition metal ions, the crystal field (CF) energy E_{CF} and the impurity Jahn-Teller (JT) energy, E_{JT} are also to be considered. The present findings imply that the dominance of one or the other of these parameters is dependent on the structural features of the crystal.

According to the EPR results, the neutral M -vacancies are stable in the tetragonal and orthorhombic phases where the MO_{12} polyhedra can be expected to be more distorted than those of rhombohedral and cubic phases. The perturbations on the oxygens, and hence of the valence band, by the absence of M -ions may lead to smaller ΔE_{dp} values when the polyhedra are more distorted so that the corresponding energy levels are continuous and overlapping with those of the valence band. When these polyhedra are

In BaTiO_3 , the changeover of $\text{Fe}^{3+}-V_{\text{O}}$ to $\text{Fe}^{3+}-V_{\text{O}}(e')$ takes place when the lattice acquires higher symmetry i.e. the coordination polyhedra are nearly undistorted (figure 8). Since the local symmetry of the $\text{Fe}^{3+}-V_{\text{O}}$ centre (C_{4v}) continues to be less than that of the surroundings, even in the cubic phase, the contribution from E_{CF} of Fe^{3+} is less significant in the above charge redistribution when compared to that of electronic deformation of the surrounding oxygen ions. Therefore, the behaviour of $\text{Fe}^{3+}-V_{\text{O}} + e' \rightleftharpoons \text{Fe}^{3+}-V_{\text{O}}(e')$ follows a similar trend to that of $V_{\text{Ba}} + e' \rightleftharpoons V'_{\text{Ba}}$. Influence of the soft modes in the former case is evident from the fact that the charge redistribution occurs not exactly at the phase transition temperature but as the system approaches the tetragonal to cubic or orthorhombic to rhombohedral phase boundary. Besides, the prevalence of $\text{Fe}^{3+}-V_{\text{O}}$ in cubic SrTiO_3 (Müller 1981) indicates that the situation in crystals with underdamped soft modes cannot be the same in BaTiO_3 with overdamped soft modes.

The variations in the valence states of transition metal ions, as illustrated by Mn indicate the important role of E_{JT} . In the tetragonal and orthorhombic phases, the TiO_6 octahedra are distorted along the c -axis so that the Ti^{4+} ion can have effective displacements. In the same surroundings, $\text{Mn}^{2+}(d^5)$ ion, with its preference to cubic symmetry shifts to a $\text{Mn}^{3+}(d^4)$ state with gain in E_{JT} , which is sufficiently large to offset the electrostatic potential, whereas, in the cubic and rhombohedral phases, the undistorted or nearly undistorted octahedral surroundings stabilise Mn^{2+} . Thus the choice of the alternatives in (16) is dictated by the symmetry of the TiO_6 octahedron. Similar conclusions can be drawn for Cu and that is why Mn and Cu are the most effective dopants in enhancing the PTCR property. The $\text{Mn}^{2+}-V_{\text{O}}$ complex does not show similar variations as $\text{Mn}^{2+}_{\text{Ti}}$ since it is locally distorted even in the cubic and tetragonal phases. $\text{Fe}^{3+}_{\text{Ti}}$, though a d^5 ion, will not behave as Mn^{2+} since Fe^{2+} is not a Jahn-Teller active ion. When the concentration of Mn is enhanced, the higher population of impurity may locally distort the lattice and stabilise part of Mn as Mn^{2+} in the tetragonal phase as well.

7. Conclusions

If one tries to identify the above mentioned soft modes with specific types of vibrations, as chemists would like to do, Last's S_2 mode of M^{2+} vibrating against the ' TiO_3 frame' (Last 1957) is one of the alternatives, the other being Slater's S_1 mode of Ti^{4+} vibrating against the oxygen octahedra (Harada *et al* 1970). Slater's S_1 mode is favoured in SrTiO_3 whereas a mixed situation of S_1 and S_2 is said to prevail in BaTiO_3 (Shirane *et al* 1970). The charge redistributions among acceptor states arising from Ba-vacancies as well as Ti-site occupants indicate the involvement of both S_1 and S_2 modes.

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The chloro-methyl exchange rule and its violations in the packing of organic molecular solids

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Abstract. Since chloro and methyl groups have nearly the same volume, they may be interchanged in a molecule without altering the crystal structure. Such isostructural behaviour is found when crystal stabilization is mainly through dispersive and repulsive interactions. Violations of this rule are, however, observed when directional forces or weak bonds are involved and the failure of complete chloro-methyl exchange in a substance like hexachlorobenzene, points to the importance of weakly attractive Cl . . . Cl interactions.

Keywords. Chloro-methyl exchange; crystal engineering; close-packing; hexachlorobenzene; Cl . . . Cl interactions.

1. Introduction

A continuing challenge in the prediction of the crystal structures of organic molecular solids is the fact that the forces which must be considered are so weak. The stablest crystal structure of most compounds is achieved by optimising a large number of subtle interactions having varying degrees of directionality and electrostatic character. These interactions are not always computationally accurately modelled in all cases. Yet there is a strong impetus to research which attempts extrapolation of organic crystal structures since such information enables a definition of new solid state reactions as well as facilitates the search for compounds with novel physical and electronic properties. Such exercises are indeed essential prerequisites in the systematic design or crystal engineering of organic structures (Thomas 1974; Desiraju 1984; Simonetta 1974).

This problem is essentially solved in those cases where the intermolecular forces are the very weakest, that is for those compounds where the crystal energy is obtained largely as the sum of the dispersive and exchange-repulsion terms (Kitaigorodskii 1973). The familiar Buckingham 6-exp type expression may be used:

$$\phi_{ij} = -Ar_{ij}^{-6} + Be_{ij}^{-C}$$

Here the potential energy ϕ_{ij} for an atom pair i, j is obtained as a function of r_{ij} and the atom potentials A , B and C . While the attractive dispersive r^{-6} term predominates at larger intermolecular distances, the repulsive exponential term is significant at shorter separations. This expression is the cornerstone of the elegant close-packing model of Kitaigorodskii (1973). The main premise here is that since dispersive and repulsive forces are isotropic, solids where only these forces are important tend to crystallize with the greatest economy of space and a maximum co-ordination number of 10 to 14.

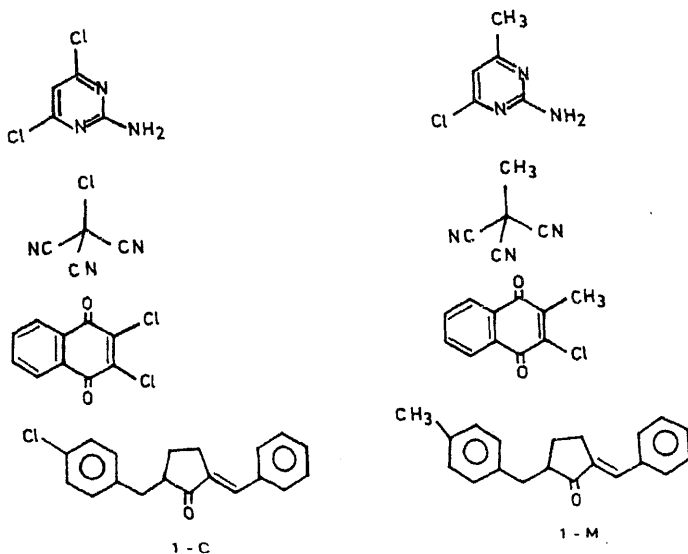
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Further, since the typical organic molecule is irregularly-shaped, the Kitaigorodskii model predicts (correctly) that space groups such as $P2_1/c$, $P\bar{1}$, $Pbca$, $P2_1$ and $P2_12_12_1$ should be especially favoured for molecular crystals. Another well-known feature of this model is that the centre of inversion is normally the only molecular symmetry element which is retained in the crystal with axes and mirror-planes being discarded in many cases.

2. The chloro-methyl exchange rule

The consequence of the Kitaigorodskii close-packing model which we shall be concerned with in this article is the so-called 'chloro-methyl exchange rule'. Since the packing of molecules is predicted in such a way that the 'voids' in one are locked into the 'protrusions' of the other, volume and shape considerations hold sway rather than electronic factors. Each non-polar substituent group of a certain volume can be exchanged for another non-polar group of a similar volume without any change in the crystal structure. Since the volumes of the chloro ($19 \text{ \AA}^3$) and methyl ($24 \text{ \AA}^3$) groups are similar, these two substituents may be interchanged in this manner. Some representative examples are shown in chart 1. An interesting example of crystal engineering is furnished by the benzyl-benzylidenecyclopentanones 1-C and 1-M shown below (Jones *et al* 1983; Theocharis *et al* 1984). Such isostructural compounds form solid solutions in all proportions. Since each of the individual compounds is photoactive in the solid state, the mixed crystals also react to form pseudo-inversion symmetry cyclobutanes (figure 1). Since the chloro-methyl exchange is valid, the different mixed crystals constitute a structural continuum between pure 1-C and 1-M.

Interestingly, the Cl-Me exchange rule may also be used to force molecular conformations into non-native ones. Consider the pair of compounds 2-C and 2-M



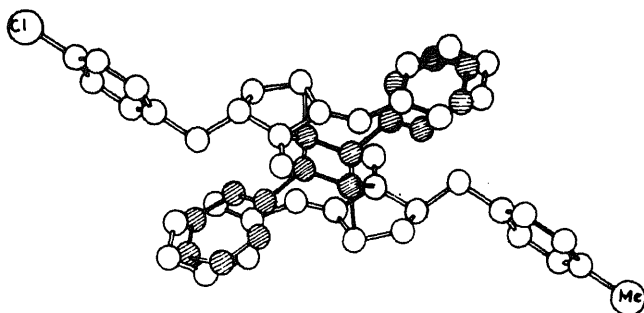


Figure 1. Formation of pseudo-inversion symmetry spirocyclobutane dimer from a crystal (solid solution) of 1-C and 1-M.

(Jones *et al* 1981). Contrary to expectation, 2-C and 2-M are not isostructural. This means that in certain cases, volume considerations are not adequate and other factors, mainly electronic must be considered. The structural differences in this pair of compounds are marked. Even the molecular conformations are different (figure 2). While 2-M adopts a photoactive modification, crystalline 2-C is photostable. Yet 2-C and 2-M will form mixed crystals (ca. 70% 2-M), isostructural with 2-M primarily as a result of conformational changes imposed upon the minor component 2-C by the dominating major component 2-M (Jones *et al* 1983; Theocharis *et al* 1984). In the mixed crystals, the 'photostable' 2-C is forced to adopt the molecular conformation, crystal structure and solid state reactivity of the 'photoactive' 2-M. It may be noted that the methyl derivative 2-M plays a crucial role in steering the structure of 2-C: 2-M mixed crystals towards that of its own structure while simultaneously incorporating increasing

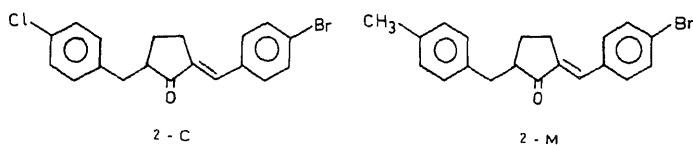
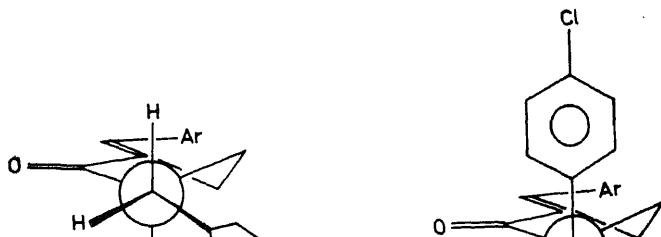


Chart 2.



amounts of a molecule (2-C) which would prefer to adopt a different structure if taken separately. Cl-Me exchange enables the adoption of an 'unfavourable' conformation and this means that the intermolecular dispersive forces involved in the stabilization of the photoactive mixed crystals evenly match the intramolecular electrostatic forces which stabilize the photostable conformation of 2-C.

3. Violations of the chloro-methyl exchange rule: Cl . . . Cl interactions

The geometrical approach of the simple close packing model which results in the Cl-Me exchange rule described above breaks down to a greater or lesser extent when directional and/or electrostatic interactions are involved. When intermolecular forces are not weak, as for example O-H . . . O hydrogen bonding, considerable deviations from close packing may be seen. Very simple hydrogen bonded compounds can have very complex crystal structures, for instance, ice, hydroquinone and trimesic acid. The prediction of crystal packings of such compounds may therefore be quite unreliable.

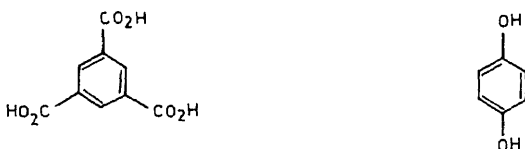


Chart 3.

The situation appears to be more tractable when very weak directional interactions are considered. A typical example is the Cl . . . Cl interaction which is manifested as short (3.2 to 3.6 Å) intermolecular contacts in the crystal structures of polychloro compounds. A recent paper (Williams and Hsu 1985) estimates the stabilization energy of such an interaction to be about 3% of a covalent Cl-Cl bond. Since these weak 'bonds' are directional, they result in deviations from Kitaigorodskii close-packing, but since they are much weaker than, say O-H . . . O hydrogen bonding, gross variations are usually not encountered. However, it seems that Cl . . . Cl interactions are sufficiently important to cause violations in the Cl-Me exchange rule.

Interactions of the Cl . . . Cl type are particularly common in the 4 A-short axis structures (β -structures) of planar chloro-aromatic compounds. Many simple polychlorobenzenes such as the ones shown below adopt this structure which is characterised by a highly overlapped stacking stabilised by C . . . C interactions (chart 4). Hexachlorobenzene (HCLBNZ) exemplifies this structural type. Figure 3 which is a stereoview of the crystal structure of HCLBNZ shows that Cl . . . Cl contacts of 3.72 Å

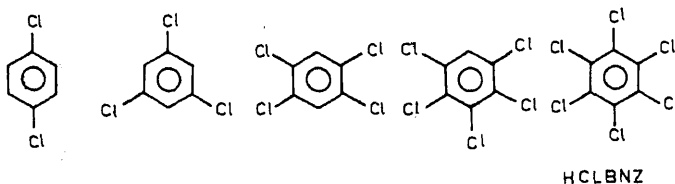


Chart 4.

result in the molecules being arranged along linear ribbons which are then stacked at the short axis separation. Successive stacks are related by two-fold screw axes and are held together by additional Cl...Cl contacts of 3.51 Å. Cl...Cl interactions therefore play a crucial role in stabilizing this structure (Sarma and Desiraju 1985).

Hence, it should be no surprise that the crystal structures of HCLBNZ and hexamethylbenzene (HMBENZ) are quite different and that the Cl-Me exchange is not valid here. In the latter structure, molecules are arranged in planar pseudo-hexagonal sheets which are stacked at 3.66 Å separation. The distance between methyl groups on adjacent molecules in a sheet is 3.90 Å, which means that normal close-packing is observed here (figure 4). These structural anomalies are not peculiar to the HCLBNZ-HMBENZ pair. In fact the Cl-Me exchange is rarely if ever applicable if *all* the Cl groups are replaced by Me groups in planar polychloro compounds. The significance of the failure of complete Cl-Me exchange in HCLBNZ is that it demonstrates that Cl...Cl interactions are attractive in nature and directional in character. In other words, chloro groups may often function as having specific, anisotropic, electronic effects rather than just as groups of a certain volume.

Another very suggestive manifestation of these effects is shown by the pair of compounds 2,2'-dichloro- and 2,2'-dimethylbenzidine. The crystal structures of these two compounds are quite different as are the molecular conformations in the solid state. While the angle between the two rings in the dimethyl compound is 86°, the corresponding angle for the dichloro derivative is only 36° with a very short non-bonded distance between the two intramolecular Cl atoms. This is an unambiguous violation of the Cl-Me rule.

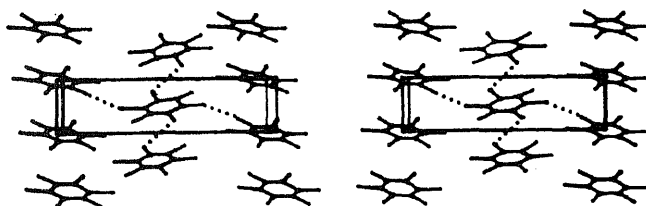


Figure 3. Stereoview of the crystal structure of hexachlorobenzene (HCLBNZ). Notice the linear ribbons interconnected by Cl...Cl contacts.

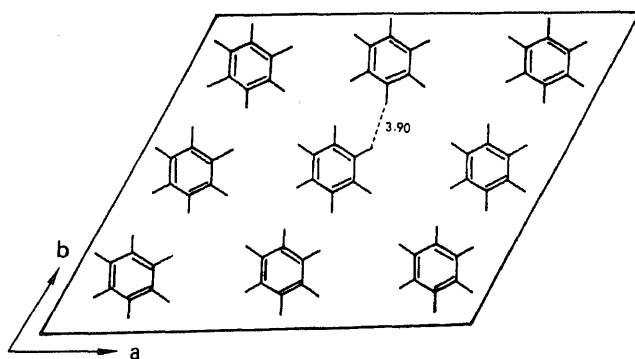


Figure 4. Projection of the crystal structure of hexamethylbenzene (HMBENZ), down the *c*-axis to the planar sheet.

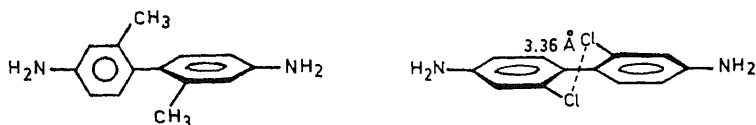


Chart 5.

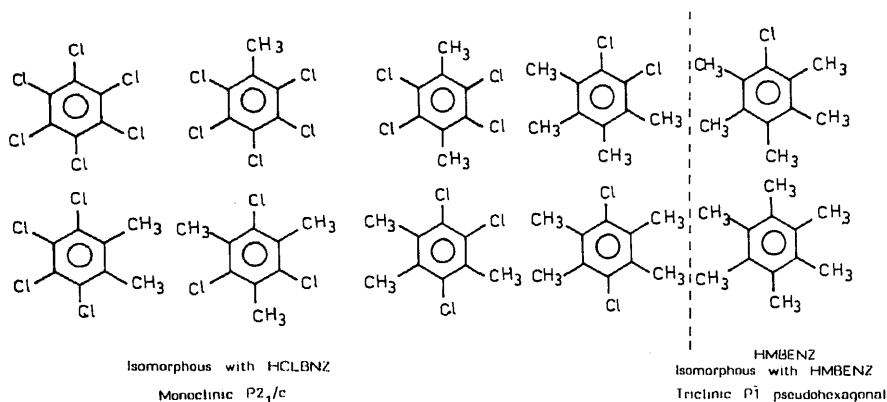


Chart 6.

Interestingly, Cl-Me exchange in HCLBNZ is valid to a limited extent in that it is possible to substitute *some* of the Cl groups by Me groups without altering the crystal structure. Thus if upto any three Cl atoms in HCLBNZ are replaced by Me, a disordered isomorphous structure results. While 1,2- and 1,4-dichlorotetramethylbenzenes also have the same disordered 4 Å structure, chloropentamethylbenzene is disordered but isomorphous with HMBENZ. These structures represent cases where the attractive Cl . . . Cl forces from the unexchanged Cl groups are countered by H . . . H repulsions which result on crowding the Me groups into those positions previously occupied by Cl, with the change in structural type occurring between one and two Cl groups. Partial Cl-Me exchange is permitted in these cases since some Cl . . . Cl interactions are still possible.

4. Conclusions

(a) The Cl-Me exchange rule follows from the Kitaigorodskii close-packing model for organic molecular crystals and is valid for, typically, large, irregularly shaped molecules or those with a small number of Cl atoms (say, one).

(b) When the number of Cl atoms per molecule is more than one and/or when the molecule becomes more planar and regular in shape, Cl-Me exchange need not apply.

(c) In these latter cases, the crystal structures are characterised by short Cl . . . Cl contacts and the anomalies in the Cl-Me exchange show up the limitations inherent in a purely geometrical approach and must be regarded as indicators for specific Cl . . . Cl interactions which cannot be incorporated into the geometrical model.

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